# Michigan's Relative Risk Task Force Report on Air Quality Issues

## **Prepared By**

Air Quality Issues Task Force George Wolff, Chair February 1999 (Second Printing July 2000)

Michigan Department of Environmental Quality
Office of Special Environmental Projects
http://www.deq.state.mi.us

John Engler, Governor Russell J. Harding, Director

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## Michigan's Relative Risk Task Force Report Air Quality Issues, February 1999

## Prepared by the Air Quality Issues Task Force

#### **Acknowledgments**

The Task Force is particularly grateful to the following individuals for their contributions to this report: Barbara Stump from Horizon Environmental for formatting the first draft of this report, Mary Ann Heindorf of the MDEQ Air Quality Division for providing many of the report's graphics, Ann Chevalier from Wayne County Air Quality Management for her input into Chapter 4, and Janice McKee from Dames & Moore for reviewing the report from a technical editor's perspective.

Office of Special Environmental Projects
Michigan Department of Environmental Quality
(Administrative and Technical Staff to the Task Force)

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Printed by Authority of Executive Order 1995-16

**Total Number of Copies Printed: 200** 

Cost per Copy: \$4.20 Total Cost: \$840.00

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## Michigan's Relative Risk Task Force Report on Air Quality Issues

#### **EXECUTIVE SUMMARY**

In July 1992, the Michigan Relative Risk Analysis project identified 24 environmental issues of concern in the state of Michigan in a report entitled *Michigan's Environment and Relative Risk*. The issues were classified into one of four relative risk categories: high-high, high, medium-high, and medium. Of the 24 issues, four air quality issues were identified. "Atmospheric transport and deposition of air toxics" was the highest ranked air issue and was ranked in the "high" category. "Photochemical smog" was ranked "medium-high," while "acid deposition" and "criteria and related air pollutants" were rated "medium" risk.

Following the release of the report, Governor John Engler directed the Natural Resources Commission to review state environmental programs and to provide recommendations to reduce the risks identified in the relative risk report to acceptable levels. The 24 risk issues were regrouped into 18 distinct categories to be assigned to separate task forces. The Air Quality Issues Task Force (Task Force) was created on June 30, 1994, and was assigned all of the air quality relative risk issues identified in the report. The Task Force was charged to:

- A. Determine whether the air quality issues identified in the report are still the appropriate issues of concern,
- B. Assess whether they pose an unacceptable public or ecological health threat now or will pose such a risk in the near future,
- C. Judge whether existing federal or state regulations and practices are sufficient to mitigate unacceptable risks, or in the case of risks that are currently acceptable, assess if present regulations are sufficient to prevent the risks from becoming unacceptable in the future, and
- D. Ascertain if additional measures are required to manage the risk to acceptable levels or to maintain them at acceptable levels.

The following conclusions and recommendations were reached by the Task Force:

- 1. Particulate Matter (PM):  $PM_{10}$  does not warrant additional control measures because compliance with national standards places it within acceptable risk. Monitoring for  $PM_{2.5}$  should begin and federal research on  $PM_{2.5}$  health effects should be encouraged.
- 2. Ground Level Ozone: Concentrations are decreasing and based on the one-hour standard, ozone does not warrant additional control measures in Michigan. Violations of the one-hour standard that occurred in western Michigan should be eliminated with the implementation of anticipated control programs in neighboring upwind states. Implementation of control programs to meet an eight-hour standard should await resolution of the necessity of this national standard.
- 3. Because of the errors in the ambient air monitoring database, an assessment of the relative risk associated with the hazardous air pollutants is not possible. The Task Force recommends that the Michigan Department of Environmental Quality makes it a high priority to collect high quality ambient air data on the hazardous air pollutants so that such an assessment can be conducted in the near future.
- 4. Persistent Hazardous Air Pollutants: Identification and control of persistent pollutants is receiving increased international and national attention. However, the lack of full understanding of the dynamics of these pollutants in the ecosystem makes it difficult to judge the acceptability of this risk. Improved monitoring, which incorporates selected watershed ecosystem evaluation, should be implemented to characterize "hot spots" and understand the air contribution to the overall risk of these pollutants.

- 5. Sulfur Dioxide: Compliance with national standards and existing regulatory programs places this within acceptable risk. Monitoring should be continued to provide data should standards be created to address control of short-term peak concentrations.
- 6. Acid Deposition: Compliance with Clean Air Act provisions and the long history of control of precursors of acid deposition place this within acceptable risk. Continued implementation of current programs and attention to the regional nature of this issue is necessary.
- 7. Carbon Monoxide: Compliance with national standards and programmatic attention to the southeastern metropolitan area place this within acceptable risk. The programs and controls in place should be continued.
- 8. Nitrogen Dioxide: Long-standing compliance with national standards and effective existing regulatory programs place this within acceptable risk.

Michigan has exercised due diligence to air quality matters. Most of the categories evaluated by the Task Force represent acceptable risk, either because monitoring indicates compliance with relevant standards or control programs are attending to the perceived risks. There are several categories which represent a potential for risk and accordingly need attention scientifically and perhaps programmatically. The state should continue to participate in regional and national efforts to protect air quality, and, to continue due diligence, should consider implementation of innovative monitoring programs.

The identification of sources and an understanding of the deposition, fate and impact of the myriad of substances found in the Great Lakes region should be a priority. Although the use of, and concentrations of, many of the persistent pollutants have declined or been eliminated little information exists on the trends and behavior of these substances in Michigan's ecosystems. The geographic extent of persistent airborne substances goes beyond the Great Lakes region.

Present and proposed pollution control programs focus on controlling introduction of individual substances while ignoring the interrelated and interdependent factors which impact overall ecosystem conditions. In order to understand the risk airborne substances represent, a program is needed which considers the broad systematic view of the impacts on the state's ecosystem.

The Trace Metals Relative Risk Task Force has recently released (April 1998) a report *Trace Metals in Michigan's Ecosystem* which provides guidance on an approach which could provide valuable information on the impact of atmospheric transport and deposition. The report proposes selection of a series of aquatic ecosystems across the state where the air, land, water, and biota components of each ecosystem would be longitudinally sampled, evaluated and compared. Examination of trace metals and other pollutants in tree rings, soil profiles and sediment profiles would reveal historical deposition rates as well as background concentrations. Lake sediments, for example, could provide not only a deposition profile but also a measure of the ecosystem response associated with the deposition. Three animal species (fish, turtles and raccoons) could be used as biomonitors to record, statewide, the accumulation and impact of persistent hazardous materials. Correlation of environmental deposition with accumulation in these species would permit an evaluation of the significance of materials introduced into the ecosystem and the response of the system to control or remediation measures.

In order to implement beneficial control measures, a program needs to be in place to evaluate whether or not the benefit is occurring and having the desired impact on the ecosystem. There is sufficient scientific uncertainty about the role of persistent hazardous air pollutants to warrant consideration of an ecologically-based monitoring program to provide data on the transport and fate of these materials in urban as well as rural areas of the state. The Task Force recommends consideration of such an approach.



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## **CHAPTER 1. INTRODUCTION**

In July 1992, the Michigan Relative Risk Analysis project identified 24 environmental issues of concern in the state of Michigan in a report entitled *Michigan's Environment and Relative Risk* (Rustem *et al.*,1992a). The issues were classified into one of four relative risk categories: high-high, high, medium-high, and medium. Of the 24 issues, four air quality issues were identified. "Atmospheric transport and deposition of air toxics" was the highest ranked air issue and was ranked in the "high" category. "Photochemical smog" was ranked "medium-high," while "acid deposition" and "criteria and related air pollutants" were rated "medium" risk.

Following the release of the report, Governor John Engler directed the Natural Resources Commission (NRC) to review state environmental programs and to provide recommendations to reduce the risks identified in the relative risk report to acceptable levels. The NRC re-grouped the 24 risk issues into 18 distinct categories to be assigned to separate task forces. The Air Quality Issues Task Force (Task Force) was created on June 30, 1994, and was assigned all of the air quality relative risk issues identified in the report. The Task Force was charged to:

- 1. Determine whether the air quality issues identified in the report are still the appropriate issues of concern,
- 2. Assess whether they pose an unacceptable public or ecological health threat now or will pose such a risk in the near future,
- 3. Judge whether existing federal or state regulations and practices are sufficient to mitigate unacceptable risks, or in the case of risks that are currently acceptable, assess if present regulations are sufficient to prevent the risks from becoming unacceptable in the future, and
- 4. Ascertain if additional measures are required to manage the risk to acceptable levels or to maintain them at acceptable levels.

#### Selection of Issues

The air quality issues discussed in the *Michigan's Environment and Relative Risk* report cover the spectrum of air quality issues (Rustem *et al.*,1992a). The fourth issue, "criteria and related air pollutants," was a catch-all category which included the issues that were not covered by the other three. Included in the fourth issue were particulate matter (PM), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), carbon monoxide (CO), acid aerosols, and visibility reduction. The reason these were categorized together was because they were not considered to present public or ecological risks in Michigan since they were being properly managed under existing federal and state regulations. Another "criteria air pollutant" is lead. This was not considered a separate issue because the elimination of leaded gasoline essentially removed lead as a ubiquitous air pollutant. Also, because the principal human exposure route for lead is no longer

through the ambient air, and because this issue has recently been the subject of a detailed assessment by the Michigan Environmental Science Board (MESB) (Fischer *et al.*,1997), it was not considered as a separate issue by the Task Force. Localized lead emissions from a relatively small number of stationary sources are covered under the air toxics category.

The Task Force determined that the way the air quality issues were categorized in the Michigan's Environment and Relative Risk report was no longer appropriate for a number of reasons (Rustem et al., 1992a). First, the United States Environmental Protection Agency (USEPA) recently proposed a five minute SO<sub>2</sub> National Ambient Air Quality Standard (NAAQS). Although the USEPA subsequently decided not to promulgate a five minute SO<sub>2</sub> NAAQS, it is still planning to increase its enforcement activity to find and eliminate five minute SO<sub>2</sub> excursions above 0.6 ppm. Since the impact of this enforcement activity in Michigan is not known, it was felt that SO<sub>2</sub> should be evaluated as a separate issue. The USEPA has also promulgated a new particulate matter NAAQS focusing on PM with a diameter of less than or equal to 2.5 micrometers (μm) (PM<sub>2.5</sub>) based on epidemiological studies which show statistical relationships with PM and premature mortality and morbidity at concentrations presently experienced throughout Michigan. Consequently, it was decided to evaluate each criteria pollutant as a separate issue. Acid aerosols and visibility are considered as part of the PM issue. The "photochemical smog" issue was renamed "ground-level ozone" because ozone is the constituent of smog that is of most concern. Furthermore, it was decided to subdivide the "atmospheric transport and deposition of air toxics" into two categories: hazardous air pollutants (HAPs) and persistent hazardous air pollutants (PHAPs). The HAPs are primarily a public health issue and include the 189 compounds identified in the 1990 Clean Air Act Amendments (CAAA) and the 250 plus compounds regulated by the Michigan Department of Environmental Quality (MDEQ). The PHAPs include approximately a dozen chemicals identified by the USEPA which have long environmental lifetimes and pose both a public health and ecosystem risk because they accumulate in the food chain of the Great Lakes' ecosystems. The issues are summarized in Table 1-1.

## DEFINITION OF UNACCEPTABLE RISK

For those air pollutants that have a NAAQS, the Task Force agreed that compliance with the NAAQS would constitute an acceptable risk, and conversely, noncompliance would constitute an unacceptable risk. However, this test of compliance was not appropriate for the new PM and ozone standards. This will be discussed in their respective chapters. For the non-criteria pollutants, the HAPs, PHAPs and acid rain, acceptable/unacceptable risk limits were identified from assessments made available by the USEPA as well as assessments from other agencies.

Table 1-1. List of air quality issues that are addressed in this report.

ISSUE	SYMBOL	MAIN CONCERNS
particulate matter	PM	premature mortality/morbidity
ground level ozone	O <sub>3</sub>	respiratory system effects
hazardous air pollutants	HAPs	general health, primarily cancer
persistent hazardous air pollutants	PHAPs	ecosystem food-chain contamination
sulfur dioxide	SO <sub>2</sub>	respiratory system effects
acid deposition		ecosystem acidification, nitrogen saturation
carbon monoxide	СО	individuals with compromised cardiovascular or
		cardiopulmonary diseases
nitrogen dioxide	NO <sub>2</sub>	respiratory system effects

## FORMAT OF REPORT

The remainder of the report will devote a chapter to each one of the identified issues. The discussions will focus on the observed historical ambient concentrations and the concentrations expected in the near future. The report will conclude with an assessment of the public health/ecological health risk that is posed by the considered pollutants.

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## **CHAPTER 2. PARTICULATE MATTER (PM)**

The 1992 Michigan Environmental Relative Risk Analysis project (Rustem *et al.*, 1992a) included particulate matter in the "criteria and related air pollutants" issue that was categorized as a medium relative risk. Since 1992, there have been a number of studies published that suggest that the public health implications of PM may be much greater than previously thought; consequently, PM is considered as a separate issue in this report.

Particulate matter is a broad classification of material that consists of either solid or liquid particles. The particles consist of many different chemical compounds. Industrial processes that emit particles include combustion, incineration, construction, mining, metal smelting, metal processing and grinding. Other sources include motor vehicle exhaust (in particular diesel-powered vehicles), road dust, wind blown soil, forest fires, ocean spray and volcanic activity. Chemical reactions also occur in the atmosphere that convert gaseous precursors such as sulfur dioxide, nitrogen oxides, and volatile organic compounds (VOCs) into particulate sulfate, nitrate and organic carbon particles, respectively.

Particulate matter in the atmosphere has been categorized according to size because of the different health impact from particles of different diameters. Particles with diameters less than about 50  $\mu m$  are classified as Total Suspended Particulates (TSP). Particles that are greater than 50  $\mu m$  in diameter do not remain in the atmosphere for appreciable lengths of time and present no health risk because they are too large to be inhaled. Particulate matter with a diameter equal to or less than 10  $\mu m$  in diameter is defined as PM $_{10}$ . Particles less than 10  $\mu m$  present a health risk because they are fine enough to be inhaled. Particles equal to or less than 2.5  $\mu m$  in diameter are called PM $_{2.5}$  and they can penetrate into the lungs during normal nose breathing. PM $_{2.5}$  is the product of combustion and chemical reactions which occur in the atmosphere. Particles in the range of 2.5  $\mu m$  to 10  $\mu m$  in diameter can penetrate into the lungs only through mouth breathing. The sub-class of PM $_{10}$  between 2.5  $\mu m$  and 10  $\mu m$  consists mostly of wind blown dust.

## PARTICULATE MATTER EFFECTS

Size is the major factor which determines which particles will enter the lungs and how deeply the particles will penetrate into the lungs.  $PM_{2.5}$  will enter deeply into the lungs; i.e., the tracheobronchial region and alveoli. Respiratory diseases can be aggravated by exposure to high concentrations of either  $PM_{10}$  or  $PM_{2.5}$ . Asthmatics, people with cardiovascular disease and chronic or acute lung disease, and the elderly are considered the populations most sensitive to the effects of particulate matter. Small but statistically significant relationships between PM concentrations and mortality have been observed. The basis and implications of these relationships will be discussed later.

Particulate matter is also responsible for soiling of surfaces and PM<sub>2.5</sub> is the most important visibility reducing component of urban and regional haze.

#### NATIONAL AMBIENT AIR QUALITY STANDARDS FOR PARTICULATE MATTER

In 1971, the USEPA established National Ambient Air Quality Standards (NAAQSs) for TSP of 260  $\mu g/m^3$  for a 24-hour average and 75  $\mu g/m^3$  for an annual geometric mean (Table 2-1). In 1987, the USEPA replaced TSP as the indicator pollutant for particulate matter with PM $_{10}$ . The 1987 PM $_{10}$  NAAQS has two components. A level of 150  $\mu g/m^3$  not to be exceeded over a 24-hour time period and a level of 50  $\mu g/m^3$  not to be exceeded as the annual arithmetic average. The 24-hour standard is based on the "expected number of exceedences" over a three-year period. A monitoring site is allowed three exceedences in three years; the fourth exceedence in a three year period is considered a violation.

Table 2-1. Historical overview of PM NAAQSs.

Year	Measure	24-Hr.	Annual
		(μg/m³)	(μg/m <sup>3</sup> )
1971	total suspended particulates (TSP)	260	75
1987	PM <sub>10</sub> (particulates with diameters ≤ 10 μm)	150	50
July 1997	PM <sub>2.5</sub>	65	15
-	PM <sub>10</sub>	150	50

On July 18, 1997, the USEPA reaffirmed the existing PM $_{10}$  NAAQS and created new PM $_{2.5}$  NAAQS (40 CFR Part 50). The new PM $_{2.5}$  NAAQS consist of an annual arithmetic mean of 15  $\mu$ g/m $^3$  and a 24-hour limit of 65  $\mu$ g/m $^3$ . Because these standards will have significant ramifications for Michigan, their impacts will be discussed. In addition, the scientific basis for the establishment of the PM $_{2.5}$  NAAQS will be examined.

## MONITORING FOR PM<sub>10</sub> IN MICHIGAN

To monitor ambient air concentrations of  $PM_{10}$ , samples are collected according to either an every sixth day, every other day or every day schedule. Previous exceedences at a site as well as its historical concentrations determine the sampling frequency. Also, every day monitoring may be required by the USEPA when violations occur. At least 75 percent of all possible data in each calendar quarter must be determined to be valid.

Figure 2-1 shows the locations of the 28 PM<sub>10</sub> monitoring stations in Michigan that were in operation during 1995. Of these, 16 are operated by industry and 12 are operated by the Michigan Department of Environmental Quality's (MDEQ) Air Quality Division, and the Wayne County Air Quality Management Division. Only ten PM<sub>10</sub> stations were in operation during 1985 whereas, in 1989, 39 sites were collecting PM<sub>10</sub> data. At present,

there are no  $PM_{2.5}$  samplers deployed in Michigan which comply with the USEPA's recently (July,1997) designated Federal Reference Method for  $PM_{2.5}$  (40 CFR Parts 53 & 58).

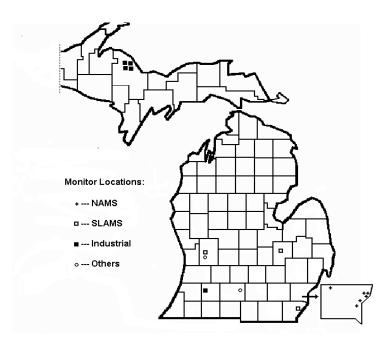


Figure 2-1. Location of PM<sub>10</sub> monitoring sites in Michigan.

ATTAINMENT/NON-ATTAINMENT STATUS OF PARTICULATE MATTER ( $PM_{10}$ ) IN MICHIGAN

In recent years, only a small region in Wayne County remained designated as nonattainment for  $PM_{10}$ . The nonattainment area was confined to a few square miles centered in River Rouge. Effective October 4, 1996, the  $PM_{10}$  nonattainment area was redesignated to attainment by the USEPA and the entire state is currently in attainment with the  $PM_{10}$  NAAQS.

## LONG TERM TRENDS IN PARTICULATE MATTER

As shown in Figure 2-2, the average arithmetic mean  $PM_{10}$  levels across the state have been decreasing since 1986 when sampling began. From the years 1993 to 1994, a slight increase in the average is noted, but this only corresponds to an increase from 20 to 23  $\mu g/m^3$ . There were 34 stations collecting data in 1993 and only 29 in operation in 1994. The data were not corrected to account for differences in the statistical sample number because it would severely limit sample size. In 1995, state-wide annual averages decreased to 22.3  $\mu g/m^3$ , just slightly greater than the 1993 value of 20 mg/m³. Nationwide trends for 1988 to 1995 show a decrease of 22 percent in the annual mean  $PM_{10}$  levels (USEPA, 1996b). In spite of the slight increase that was observed during 1994, levels in Michigan also show a decrease of 20 percent over the 1988-95 time period.

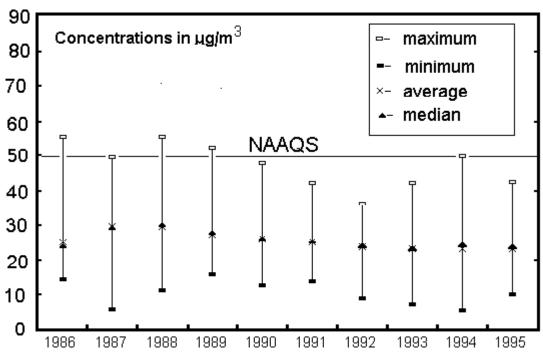


Figure 2-2. Range of annual arithmetic means for PM<sub>10</sub> levels at all sites in Michigan.

Of the maximum readings in Figure 2-2, during 1986, only one monitor, at the Dearborn Salina location, recorded an annual arithmetic mean greater than 50  $\mu g/m^3$ . The maximum  $PM_{10}$  levels during 1987, 1988 and 1989 were also logged by the same Dearborn monitor. In 1987, this monitor logged an annual arithmetic average that equaled the NAAQS. In 1988, values of 52  $\mu g/m^3$  and 55  $\mu g/m^3$  were measured by the Dearborn monitor. In 1989, an annual arithmetic mean of 52  $\mu g/m^3$  was measured at this location. Finally, in 1990, annual levels in Dearborn were below the standard when 48  $\mu g/m^3$  and 44  $\mu g/m^3$  were measured by two monitors in operation at the site. Monitoring at the Salina location in Dearborn was stopped when the land was developed in 1990, and the monitoring station was relocated about 500 ft away to a location at 2842 Wyoming in Dearborn. During 1992 and 1993, annual averages at this site were 37  $\mu g/m^3$  and 42  $\mu g/m^3$  respectively. In 1994, an annual average of 49  $\mu g/m^3$  was recorded at this site. The 1995 annual average for this site decreased to 41.9  $\mu g/m^3$ .

Figure 2-3 illustrates the trends in the 24-hour  $PM_{10}$  values in Michigan. In 1992 a value of 494  $\mu g/m^3$  was measured at an industrial site in Bay City on June 17. However, severe weather with excessive wind conditions occurred on this date and the MDEQ requested it be considered an "exceptional event" under federal criteria. This incident skewed the average slightly higher for all the sites in Michigan in 1992. Other than this incident, average 24-hour levels have been relatively constant from 1987 to 1995 at about 70  $\mu g/m^3$ . Maximum values in 1995 were elevated due to two exceedences that occurred in Dearborn on March 14 and 15, 1995, reaching levels of 183 and 159  $m g/m^3$ , respectively. This event was believed due to particulate control equipment failure at a stationary source near the monitor site.

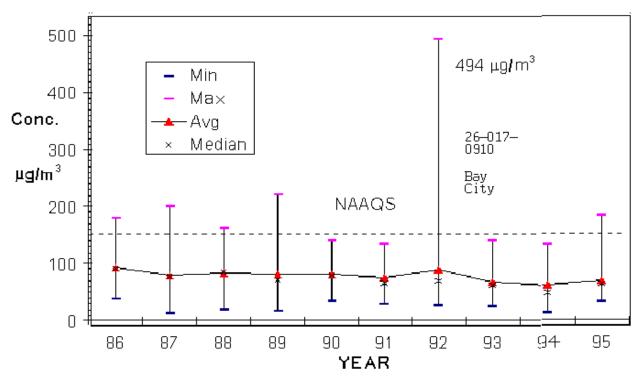


Figure 2-3. Range of maximum 24-hour PM levels at all sites in Michigan.

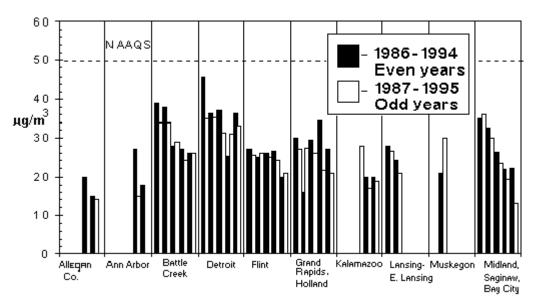


Figure 2-4. PM<sub>10</sub> levels by Metropolitan Statistical Areas (mean of annual arithmetic average).

Figure 2-4 compares the mean of the annual arithmetic average  $PM_{10}$  levels for all Metropolitan Statistical Areas (MSA's) where monitoring was conducted. The highest  $PM_{10}$  levels have been observed in the Detroit area, with Saginaw/Midland/Bay City also being elevated during the mid 1980's. The figure shows quite dramatic and

consistent reductions in  $PM_{10}$  levels detected at all sites except Muskegon. However, Muskegon's levels were low enough so  $PM_{10}$  sampling is no longer required by the USEPA.

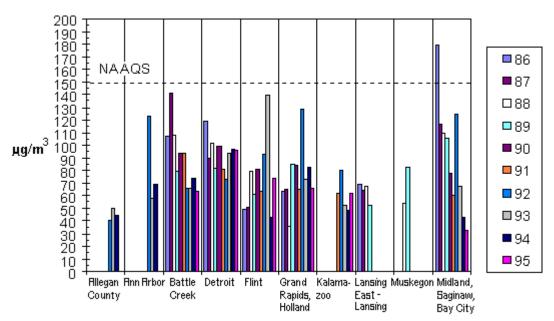


Figure 2-5. PM<sub>10</sub> levels by Metropolitan Statistical Areas (mean of 24-hour values).

Average peak 24-hour  $PM_{10}$  levels were calculated for all MSA's as shown in Figure 2-5. At various times during the previous ten years, the average values for each MSA have peaked. While almost all MSA's show downward trends, the trends of the 24-hour peaks are less representative of the overall improvement in  $PM_{10}$  air quality because the 24-hour annual peak is an extreme value.

ASSESSMENT OF THE NEW  $PM_{2.5}$  NATIONAL AMBIENT AIR QUALITY STANDARDS

In its July 1996 Staff Paper (USEPA, 1996d), the USEPA recommended retaining the existing  $PM_{10}$  NAAQS and adding a new annual and 24-hour  $PM_{2.5}$  NAAQS. It proposed that the annual  $PM_{2.5}$  NAAQS be in the range of 12.5 to 20  $\mu g/m^3$  and that the 24-hour NAAQS be in the range of 18 to 65  $\mu g/m^3$ . Subsequently, the USEPA Administrator reviewed the recommendations and on July 18, 1997, announced the levels for the NAAQSs shown in Table 2-1 (40 CFR Part 50).

With the new annual  $PM_{2.5}$  NAAQS, the number of counties in the nation violating an annual PM NAAQS is estimated to increase from 11 to 283. The USEPA projects the following Michigan counties will be in nonattainment: Wayne, Oakland, Lapeer, Macomb, Monroe and St. Clair. The MDEQ projected that Wayne, Monroe, Calhoun Kent and Saginaw Counties will be in nonattainment. It should be noted, however, that both projections are just rough estimates because at present the MDEQ has no  $PM_{2.5}$ 

monitoring sites in Michigan. Since the proposed  $PM_{2.5}$  NAAQS is significantly more stringent than the existing  $PM_{10}$  NAAQS, it is very likely that at least these southeast Michigan counties and perhaps other areas that meet the  $PM_{10}$  NAAQS by only a small margin will be in nonattainment with respect to the annual  $PM_{2.5}$  NAAQS.

Although individual PM health effect studies have focused on a variety of endpoints, epidemiology studies that focused on human mortality were the primary impetus for the USEPA proposing a new PM $_{2.5}$  NAAQS. Most of these epidemiology studies used measurements of TSP, PM $_{10}$ , or some PM $_{2.5}$  surrogate because direct measurements of PM $_{2.5}$  were not available. There were two types of PM-mortality studies cited by the USEPA. The first was the short-term, acute mortality studies which compared daily PM concentrations and the daily mortality in about two dozen locations around the U.S. One of the locations was the Detroit area (Schwartz, 1991). After accounting for the effects on mortality of such things as season, day of the week, meteorology, etc., the remaining statistical relationship between daily PM and daily mortality was quantified. Although this relationship varied from location to location, the average value was on the order of a four percent increase in daily mortality with a 50  $\mu$ g/m $^3$  increase in PM $_{10}$  concentrations.

The second type of epidemiological study is the long-term prospective cohort study where the health status of certain groups (cohorts) of individuals is followed for a number of years in various locations around the country. In these studies, the annual mortality rate in a given location is related to the annual average  $PM_{10}$  or  $PM_{2.5}$  concentration after the mortality rates have been adjusted for smoking and some other potentially confounding variables. Of the three studies reported in the literature, two show a positive relationship between annual mortality and PM and attribute two to three times the number of deaths to PM as the short-term acute effect studies. The third study shows no PM-mortality relationship but the USEPA dismissed this study for a number of reasons including its lower statistical power (smaller sample size).

The USEPA uses higher mortality estimates from the two studies to conclude that there are premature deaths due to chronic exposure to PM in addition to the deaths due to acute exposures identified in the daily mortality studies. In addition, the USEPA also concluded that the mortality was due to  $PM_{2.5}$  rather than the coarse fraction of the  $PM_{10-2.5}$  or the total  $PM_{10}$ .

The scientific basis for the USEPA's conclusions was reviewed and assessed by a 21-member panel of independent scientists from the USEPA's Clean Air Scientific Advisory Committee (CASAC) (Wolff, 1996). Because of the acceptance that  $PM_{10-2.5}$  and  $PM_{2.5}$  are different pollutants, there was a consensus that a new  $PM_{2.5}$  NAAQS be established, with nineteen CASAC members endorsing the concept of a 24-hour and/or an annual  $PM_{2.5}$  NAAQS. However, there was no consensus on the level, averaging time, or form of a  $PM_{2.5}$  NAAQS. The CASAC members' opinions concerning the level of an annual standard can be classified into several broad categories. Two CASAC Panel members supported a NAAQS as low as 15  $\mu g/m^3$ . Five CASAC members supported a number between 20 - 30  $\mu g/m^3$ . Eight members did not think an annual

PM<sub>2.5</sub> NAAQS was warranted at all. The remaining six CASAC members endorsed the concept of a annual PM<sub>2.5</sub> NAAQS but declined to endorse a specific range or level; however, most of the members who declined to recommend a range provided comments for the record which indicate they generally favor a level significantly higher than the 15  $\mu$ g/m³ chosen by the USEPA.

The diversity of opinion expressed by the CASAC members reflected the many unanswered questions and large uncertainties identified by CASAC. Most CASAC members were influenced, to varying degrees by these unanswered questions and uncertainties. The concerns ranged from doubting that the USEPA correctly identified PM<sub>2.5</sub> as a causal agent to questioning the validity of the statistical models that were used in the epidemiological studies. The diversity of opinions expressed by CASAC members clearly underscores that there is no scientific certainty that PM<sub>2.5</sub> is a health risk at ambient concentrations thought to exist in Michigan today. Similar conclusions were reached by the Michigan Environmental Science Board (MESB) (Fischer *et al.*, 1997).

## CONCLUSIONS AND RECOMMENDATIONS

At present, all locations within Michigan are attaining the existing  $PM_{10}$  NAAQS, and the trend in  $PM_{10}$  concentration continues downward. This trend should continue in the near future because of the implementation of other air pollution control programs currently in effect that will continue to reduce  $PM_{10}$  emissions and the emissions of gaseous PM precursors. Consequently  $PM_{10}$  does not appear to pose an unacceptable public health risk in Michigan and new control initiatives targeting  $PM_{10}$  are not warranted.

For PM<sub>2.5</sub>, the situation is not as simple. The CASAC review demonstrated that there is no scientific consensus on the degree of public health risk posed by PM<sub>2.5</sub>. Furthermore, the Air Quality Issues Task Force (Task Force) is lacking usable data because Michigan has not established a monitoring program to evaluate this parameter. On balance, more of the CASAC members favored a PM<sub>2.5</sub> NAAQS at level above those which the USEPA has chosen. These members favored a PM<sub>2.5</sub> NAAQS roughly of equivalent stringency as the current PM<sub>10</sub> NAAQS (approximately 25-30  $\mu$ g/m³) (Wolff, 1996). At such a level, Michigan would likely be in attainment and the threat posed to public health would be perceived to be acceptable. However, unless the new PM<sub>2.5</sub> NAAQS are overturned by Congress or in the courts, Michigan will be required under federal law to implement additional emission control programs in any areas found to be in nonattainment.

At this time, the Task Force recommends that Michigan not initiate new control programs that target  $PM_{2.5}$  or  $PM_{2.5}$  precursors until they are required by federal law. Certain areas of the state are likely to be in nonattainment with the annual  $PM_{2.5}$  NAAQSs. However, according to the USEPA's annual  $PM_{2.5}$  NAAQS implementation schedule, compliance is not expected to be mandated until the year 2005, which is well after the completion of the next USEPA/CASAC review cycle, that will begin in 1998.

The Task Force does recommend, however, that Michigan begin  $PM_{2.5}$  sampling as soon as possible. In addition, it also recommends that Michigan encourage the USEPA to accelerate its  $PM_{2.5}$  health effects research program so that the uncertainties and many unanswered questions raised by CASAC and others are addressed before the next CASAC PM NAAQS review is completed in 2002.

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#### CHAPTER 3. GROUND-LEVEL OZONE

The 1992 Michigan Environmental Relative Risk Analysis project (Rustem *et al.*,1992a) included ground-level ozone as a separate issue that was categorized as a medium-high relative risk. Since 1992, there have been a number of studies published that suggest that the public health risks of ozone may occur at concentrations lower than previously thought. Consequently, ozone is considered as a separate issue as well in this assessment.

Ozone is a colorless gas that is formed in the lower atmosphere from photochemically-initiated reactions involving nitrogen oxides ( $NO_x$ ) and volatile organic compounds (VOCs). Sources of nitrogen oxides are any combustion source and they are discussed in more detail in the nitrogen dioxide chapter. The primary sources of VOCs include motor vehicle exhaust, gasoline vapors, solvents, and degreasing agents. Important natural sources of VOCs are vegetation and trees. Sunlight initiates the chemical reactions and high temperatures enhance the chemical reactions that form photochemical smog of which ozone is the principal component of concern, (photochemical smog itself is a mixture of many gases and particles). Because ample sunshine and warm temperatures are a prerequisite for high concentrations of ozone, concern over ozone is generally limited to the sunny days when the temperature approaches or exceeds  $85^\circ$  Fahrenheit.

The ozone that is contained in photochemical smog is formed primarily in the layer of air which extends from the ground up to a few thousand feet, and is also known as "tropospheric" ozone or "ground level" ozone. Another layer of ozone, formed in the stratosphere (7 to 30 miles above the earth's surface and not in the breathing zone) from natural processes, is responsible for shielding the earth's surface from harmful ultraviolet rays from the sun that cause skin cancer. Stratospheric ozone is sometimes referred to as "good" ozone while ground-level ozone is referred to as "bad" ozone. They are chemically identical. The only difference is where they are formed. This report deals only with ground-level ozone.

Ground-level ozone can be transported long distances under favorable meteorological conditions. For example, it has been well documented that air arriving in southwestern Michigan can already contain ozone concentrations exceeding the National Ambient Air Quality Standard (NAAQS) due to VOC and  $NO_x$  emissions in the Milwaukee/Chicago areas. Consequently, reducing emissions in southwestern Michigan will not solve this situation.

## **OZONE EFFECTS**

Recent studies indicate that there is a continuum of biological responses among individuals engaged in moderate physical activity down to background concentrations of ozone (0.03 - 0.05 parts per million [ppm]) (Wolff, 1995). These responses include temporary reduced performance on lung function tests, cough and chest pains. No responses are observed in individuals not engaged in moderate physical activity when

the ozone concentration is below 0.50 ppm. In addition, there appears to be a relationship between ozone concentrations and hospital/emergency room admissions for respiratory diseases, and this relationship does not appear to have a threshold concentration (USEPA, 1996a).

There also appears to be a continuum of responses for vegetation at any level above background concentrations. Ozone can inhibit photosynthesis, alter carbon allocation, and interfere with myzorrhizal formation on tree roots. Disruption of these physiological processes can suppress the growth of vegetation including crops and trees. At high concentrations, ozone can cause visible damage to leaves of certain species (USEPA, 1996a).

## THE ONE-HOUR NATIONAL AMBIENT AIR QUALITY STANDARD FOR OZONE

Until 1997, the only NAAQS for ozone was a one-hour average concentration of 0.12 ppm, not to be exceeded on more than three days during any three consecutive year period. Therefore, the average number of exceedences over the past three years needed to be less than or equal to one in order to meet the NAAQS for ozone.

In the 1992 Relative Risk project (Rustem *et al.*, 1992a) photochemical smog was ranked as a "medium-high" priority based largely upon the accompanying review contained in a White Paper (Rustem *et al.*, 1992b) (Wolff, 1992). At that time, it was acknowledged that there were three ozone nonattainment areas (southeast Michigan, Muskegon, and Grand Rapids) in the state, but it was generally perceived that regulations in place and the recent studies LMOS (LADCO, 1995) and SEMOS (Wolff *et al.* 1993), would be sufficient to bring all three areas into attainment in the near future. However, caution was advised because health effect studies were beginning to suggest that health effects may be occurring at concentrations below the one-hour NAAQS.

Since that time, a number of things have occurred to complicate the issue. First, in April 1995, southeast Michigan was redesignated to attainment following four summers without a violation of the NAAQS. However, a violation at two different sites occurred in the summer of 1995. As a result, southeast Michigan had to implement a measure from its Contingency Plan (MDEQ, 1996a). The measure selected was the introduction of low Reid Vapor Pressure (RVP) gasoline of 7.8 pounds per square inch (psi) during the ozone season. That measure went into effect July 1, 1996. There were no violations in southeast Michigan during the summers of 1996 or 1997.

In southwest Michigan, the summer of 1994 was the third consecutive violation free summer which qualified both the Muskegon and Grand Rapids areas for redesignation. As a result, the state applied for redesignation but while the USEPA was reviewing the application, the Muskegon area experienced violations. As a result, only Grand Rapids was redesignated.

In 1996, violations of the ozone one-hour NAAQS were experienced in Grand Rapids, Muskegon, Holland, and Ludington. The USEPA, however, is not requiring any additional control measures to be implemented by the state in these areas because of the realization that the ozone is formed from emissions on the southern and western shores of Lake Michigan. It is anticipated that when additional emissions controls are implemented in northern Indiana, northwestern Illinois, and southeast Wisconsin, they will be sufficient to bring these western Michigan communities into compliance with the one-hour NAAQS. In fact, in1997, there were no exceedences of this NAAQS

## OZONE TRANSPORT AND ASSESSMENT GROUP (OTAG)

In response to the chronic ozone nonattainment problems experienced in the Northeast and in the Chicago-Milwaukee area which were blamed, in part, to be due to ozone transported from upwind states, the USEPA required the 37 most eastern states to participate in a two year long regional modeling/control strategy development exercise which became known as the Ozone Transport and Assessment Group (OTAG, 1997). The purpose of the exercise was to determine a regional strategy that, when applied across the 37-state region, would reduce ozone transport enough so that the chronic nonattainment areas would be able to come into attainment.

The results of the regional modeling, however, showed that much of what was thought to be actual transport of ozone molecules was transport of meteorological conditions that were conducive for ozone formation. In addition, the results inferred that the atmospheric lifetime of ozone molecules is inversely proportional to the amount of precursor emissions they encounter in transit. In a series of model runs where emissions in the Midwest (including Michigan) were greatly reduced but emissions in the Northeast were held constant, there was very little decrease of ozone in the Northeast. At best, it showed an ozone decrease in the Northeast corridor of about 0.002 ppm - 0.004 ppm, which is considerably less than the uncertainty of the model predictions. Other model runs showed that the most efficient way to reduce ozone in the Northeast is to apply the control measures there. Ongoing modeling by the Michigan Department of Environmental Quality (MDEQ), confirm the OTAG modeling results (MDEQ, 1998).

Despite these results, the USEPA and the northeast states remain unconvinced that the Midwest does not significantly contribute to nonattainment in the Northeast. Consequently, the USEPA proposed rules that will impose drastic regional  $NO_x$  reductions on most of the OTAG states including the southern half of lower Michigan (40 CFR Part 52). The final USEPA rule is expected in the fall of 1998 with a State Implementation Plan due one year later.

#### OZONE MONITORING IN MICHIGAN

During the past ten years, the number of ambient monitoring sites for ozone has ranged from 19 in 1986 to 38 stations operating during 1991, including some monitors that were part of the Lake Michigan Ozone Study (LMOS). All the stations have been operated by the USEPA, state of Michigan and Wayne County. During 1995, the state and local agencies operated 25 ozone ambient monitoring stations (as seen in Figure 3-1). Figure 3-1 also shows the locations of three USEPA sites and one station that is operated by the state of Indiana. In addition, on May 24, 1995, Wisconsin began operation of an ozone monitor on the Badger Ferry, which travels from Ludington, Michigan to Manitowoc, Wisconsin. The monitor is situated on the ferry, approximately 27 meters above the lake level. These data will supply information about ozone concentrations coming into the state. As a contribution to the regional monitoring program being conducted by the other Great Lakes states, Michigan is expanding the ozone monitoring site in Holland to a photochemical assessment monitoring station (PAMS). In addition to sampling for ozone, beginning in June 1996, the Holland site will monitor for ozone precursors (VOCs, carbonyls, and NO<sub>x</sub>).

Maximum ozone concentrations are usually measured downwind from metropolitan areas that generate precursor emissions. These stations are typically 10 to 30 miles from the edge of the urban area. Of the stations that are currently in operation, the sites at Rose Lake, Otisville, Parnell/Grattan Township, New Haven, Port Huron, and Algonac are located to detect maximum concentrations of ozone contained within urban scale air masses.

## AMBIENT AND EMISSION TRENDS

Ambient ozone generally suggest a slightly downward to a flat trend in ozone concentration across the state. Because the MDEQ's report focuses mainly on trends in the first or second highest one-hour maximum concentration in a given year, they should be interpreted cautiously. The first and second annual maximum are extreme values and exhibit considerable year to year variability. These measures are dictated by extreme, relatively rare meteorological events. A more representative picture of long-term trends may be obtained by examining the number of exceedences each year. The MDEQ visually examined the trend in the composite statewide exceedences but drew no conclusions because of the impact of 1988. The summer of 1988 was an abnormally hot summer with record temperatures occurring during the time when the RVP of the gasoline sold in Michigan was at its maximum.

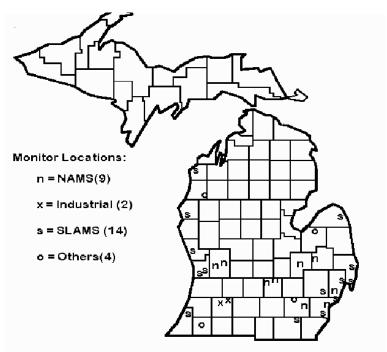


Figure 3-1. Air quality monitors for O<sub>3</sub> active in 1995.

If the data from 1988 are set aside, a much different picture emerges. In Figures 3-2 and 3-3, the data are reported by region without 1988 and a linear regression line is fitted for each region. Figure 3-2 shows the trends in southeast Michigan subdivided into Oakland, Macomb, St. Clair, Wayne Counties and the Lansing and Flint areas. All trends are negative and suggest that southeast Michigan has reached or attainment. Similar data are plotted in Figure 3-3 for the Muskegon and Grand Rapids monitors. This graph suggests that Muskegon will achieve attainment within a few years and that the trend in Grand Rapids is flat but the mean number of annual exceedences is about one.

Consistent with these downward trends is the fact that all three areas recently qualified to be redesignated and two of them were approved. Furthermore, the redesignation proposals submitted to the USEPA demonstrated that the improvements in ozone air quality were due to decreased emissions of ozone precursors and that the decreasing trends in emissions were projected to continue through the year 2005.

## NEW NATIONAL AMBIENT AIR QUALITY STANDARD FOR OZONE

The USEPA announced on July 18, 1997 (40 CFR Part 50) a new primary and secondary ozone NAAQS. The new NAAQS is an eight-hour average of 0.08 ppm. To determine attainment status, an area will calculate the average of the fourth highest eight-hour concentration for each of the last three years for each site. If that average at any site exceeds 0.084 ppm, the area will be in violation of the NAAQS. Under this proposed NAAQS, three counties in southeast Michigan, and eight counties in western Michigan that have ozone monitors would be nonattainment (based on 1995 through 1997 air quality data). This probably underestimates the spatial extent of what will be

nonattainment in Michigan, however, because it is likely that additional counties that presently do not have ozone monitors will become nonattainment.

# ASSESSMENT OF THE NEW EIGHT-HOUR OZONE NATIONAL AMBIENT AIR QUALITY STANDARDS

In its August 1995 Staff Paper, the USEPA recommended replacing the current onehour ozone NAAQS with an eight-hour NAAQS in the range of 0.07 - 0.09 ppm with one to five allowable exceedences per year (USEPA, 1996a). Subsequently, the USEPA Administrator reviewed the staff recommendations and on July 18, 1997, established primary and secondary eight-hour NAAQS for ozone of 0.08 ppm (USEPA, 1996a). To determine attainment status, an area will calculate the average of the fourth highest eight-hour concentration for each of the last three years for each site. If the average of any site exceeds 0.084 ppm, the area will be in violation of the NAAQS. Under the new NAAQS, the USEPA projects that 11 Michigan counties (Macomb, St. Clair, Wayne, Kent, Kalamazoo, Ottawa, Muskegon, Allegan, Benzie, Cass, and Mason) would be nonattainment. However, the MDEQ estimates that the number of nonattainment counties not complying with the eight-hour NAAQS could be as high as 34. In any event, the new NAAQS is significantly more stringent than the one-hour NAAQS. An eight-hour NAAQS of 0.09 ppm ozone with three or four allowable annual exceedences would be approximately equal in stringency as the one-hour NAAQS.

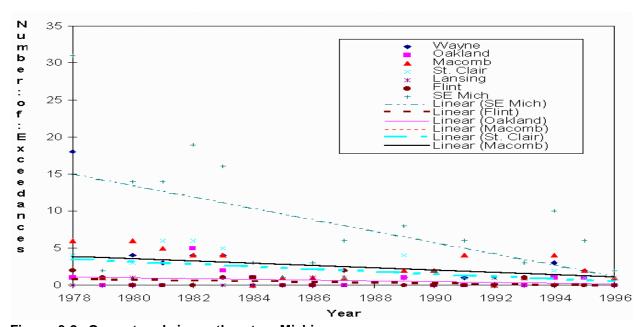


Figure. 3-2. Ozone trends in southeastern Michigan.

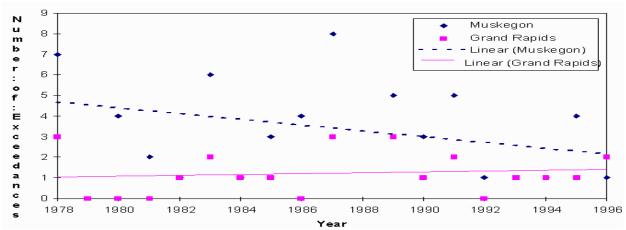


Figure. 3-3. Ozone trends in western Michigan.

The USEPA's decision to change to the new standard followed an extensive review of the scientific basis of the standard by the USEPA's Clean Air Scientific Advisory Committee (CASAC) (Wolff, 1995b). It was the consensus of the CASAC members that an eight-hour standard was more appropriate for a human health-based standard than a one-hour standard.

CASAC felt that the weight of the health effects evidence indicated that there is no threshold concentration for the onset of biological responses due to exposure to ozone above background concentrations. CASAC noted however, that a biological response does not necessarily imply an adverse health effect. Nevertheless, it concluded that the paradigm of selecting a standard at the lowest-observable-effects-level and then providing an "adequate margin of safety" is no longer operable. It further recommended that the USEPA use risk assessments to identify an appropriate level for a NAAQS.

To conduct the risk assessments, the USEPA had to identify the populations at risk and the physiological responses of concern, develop a model to estimate the exposure of this population to ozone, and develop a model to estimate the probability of an adverse physiological response to the exposure. The USEPA selected a small segment of the population, "outdoor children" and "outdoor workers," particularly those with preexisting respiratory disease as the appropriate populations with the highest risks.

Based on the results of the risk assessments presented in the Staff Paper (USEPA, 1996a) and an acknowledgment that all the uncertainties cannot be quantified, the CASAC concluded that there is no "bright line" which distinguishes any of the proposed standards or the present standard (either the level or the number of allowable exceedences) as being significantly more protective of public health. It further stated that the selection of an appropriate level within the proposed range (even including the one-hour NAAQS) is strictly a policy call.

Although, the CASAC could see no "bright line" to use as a guide in selecting the numerical value of an NAAQS, some of the members did express personal preferences for the level of the eight-hour NAAQS. Of the ten members involved in the review of the

primary NAAQS, all endorsed an eight-hour standard and all endorsed multiple exceedences. Three members recommended 0.08 ppm. Three other members recommended 0.09 ppm, one member said there was no difference between 0.08 ppm or 0.09 ppm, and another said there was no difference between 0.09 ppm or 0.10 ppm. Two other members indicated that it is a policy decision because the science has not shown any of the alternatives that are being considered as being more protective of public health than any other. This can be interpreted as a vote of support for an eight-hour NAAQS equivalent in stringency to the current NAAQS.

Because there is no apparent threshold for responses and no "bright line" in the risk assessment, a number of CASAC members recommended that an expanded air pollution warning system be initiated so that sensitive individuals can take appropriate "exposure avoidance" behavior. Since both southeastern and southwestern Michigan already have an infrastructure in place to designate "ozone action days" when voluntary emission reduction measures are put in place, this idea would be easy to implement.

In summary, although the CASAC members' opinions differed, none supported the lower end of the USEPA recommendations, and the majority of the members stated a position which included an eight-hour NAAQS of equivalent stringency to the present one-hour NAAQS of 0.12 ppm.

As mentioned earlier, the new eight-hour ozone NAAQS will result in 11 to 34 non-attainment counties in Michigan. In addition, modeling being conducted by the MDEQ (1998) indicates that even with the drastic  $NO_x$  reductions proposed by the USEPA to reduce ozone transport; neither southwestern or southeastern Michigan will comply with the new NAAQS. The modeling further suggests that an across the board  $NO_x$  reduction strategy is not a cost-effective way to reduce ozone in Michigan and in some areas, it actually produces ozone increases.

## CONCLUSIONS AND RECOMMENDATIONS

Ozone concentrations throughout the state are decreasing and based on emission inventory projections they should continue to decline in the near future. Maintenance plans that are in effect will insure that precursor emissions will not increase in the future. Because of the improvements in air quality, Muskegon, Allegan, Oceana and Mason counties remain the only counties in the state still effected by one-hour NAAQS. While trend lines suggest that these counties will attain the one-hour NAAQS in a few years, it is generally acknowledged that their high ozone is due to transport from the Chicago/Milwaukee area and that local emission reductions would not greatly reduce ozone. Additional measures beyond managing the programs in place would not be necessary.

However, even though public health benefits for a new eight-hour standard at 0.08 ppm have not been demonstrated, the USEPA has adopted it and numerous counties in southern Michigan do not meet it. Additional, widespread emission reductions of precursor emissions will be necessary for these counties to come into compliance.

Modeling conducted by the MDEQ and the Ozone Transport Assessment Group indicates that the drastic  $NO_{x}$  reductions proposed by the USEPA for sources in Michigan will neither result in compliance with the new eight-hour NAAQS nor contribute to measurable reductions of ozone transported to the northeast U.S. Furthermore, the modeling indicates that such a  $NO_{x}$  reduction strategy is not appropriate for either southeast or southwest Michigan.

At this point, the Task Force recommends that Michigan not initiate any new control programs that target  $O_3$  precursors until they are required by federal law to do so. However, this could happen as early as the year 1999 if Michigan is required to implement the USEPA's regional transport strategy for the OTAG states (40 CFR Part 52).

### CHAPTER 4. HAZARDOUS AIR POLLUTANTS

The 1992 Michigan Relative Risk Analysis project (Rustem et al., 1992a, Wolff, 1992) included an issue called "atmospheric transport and deposition of air toxics" as a separate issue that was categorized as a high relative risk, primarily because of a number of chemicals that have long lifetimes in the environment and can bioaccumulate. Because of this, the Governor's Relative Risk Air Quality Issues Task Force (Task Force) decided to subdivide the "atmospheric transport and deposition of air toxics" into two categories: hazardous air pollutants (HAPs) and persistent hazardous air pollutants (PHAPs). The HAPs, as referred in this report, include both the 188 compounds identified in section 112(b) of the federal Clean Air Act (CAA) as amended in 1990 and the over 750 compounds with screening levels developed under Michigan's air toxics rules for new or modified sources that are required to obtain Michigan installation permits. Michigan's air toxic rules are applicable to any constituent emitted except for 40 that have been specifically exempted. Consequently, the list of 750 substances for which screening levels have been developed and that Michigan lists as air toxics will increase if a permit application identifies the release of substances which are not either already on the list or exempted from the rule. The PHAPs include the approximately one dozen chemicals identified by the USEPA which have long environmental lifetimes and pose both a public health and ecosystem risk not due to direct inhalation, but because they accumulate in the food chain of the Great Lakes ecosystems.

A wide variety of substances are classified as HAPs or PHAPs. The exact compounds and substances included in this category are determined by the various state and federal regulations that address these materials, as well as their potential toxic effects. In general, HAPs and PHAPs can be divided into inorganic compounds, organic compounds and other substances. Inorganic compounds include toxic metals such as arsenic (As), beryllium (Be), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn), and non metals such as chlorine and hydrochloric acid. The organic toxics classification includes some volatile organic compounds (VOCs), some carbonyl compounds, polynuclear aromatic hydrocarbons (PAH's or PNA's), pesticides, and polychlorinated biphenyls (PCB's). The other substances include asbestos, coke oven emissions and radionuclides such as radon. This Chapter will focus on HAPs while Chapter 5 focuses on PHAPs.

Extensive monitoring, both geographically and temporally, for airborne toxics has not been performed throughout Michigan, although there is a monitoring history for HAPs in southeast Michigan and some other selected urban areas. The analytical methodology is difficult to perform and requires more expensive instrumentation as compared to the methods used for measuring the criteria pollutants. The many different chemical compounds that make up HAPs require the use of assorted analytical methods, further increasing the time and cost burdens that are associated with this type of monitoring. In spite of these difficulties, increasing commitments are being made nationwide to augment ambient monitoring for airborne toxics.

An understanding of the legislative history of the regulation of HAPs will provide an idea of the different definitions of toxic compounds that are used, describe the monitoring required, and provide insight into the evolution of air toxic monitoring in Michigan. The current status of monitoring for selected toxic compounds in the state is discussed. Lastly, two HAP studies conducted in southeast Michigan are discussed.

### FEDERAL LEGISLATIVE HISTORY

Before the promulgation of the Clean Air Act Amendments (CAAA) in 1990, the National Emission Standards for Hazardous Air Pollutants (NESHAPs) program was the principle federal program for regulating HAPs. However, throughout the history of the NESHAPs program, regulations were developed for only eight pollutants; arsenic, asbestos, benzene, beryllium, mercury, radionuclides, radon and vinyl chloride. The CAAA of 1990 required the regulation of 189 substances and imposed technology-based standards for reducing emissions of these substances.

The CAAA also proposed a standard for chemical manufacturing companies which requires reductions in the emissions of 189 HAPs. By 1998, this standard will reduce HAP emissions by 80 percent. In addition, many of the HAPs chemicals are also VOCs which contribute to the formation of ozone and may be reduced or controlled by CAAA programs designed to reduce ozone levels.

Another federal program which will impact Michigan is the Great Waters Program. The Great Waters Program was established by section 112(m) of the 1990 CAAA. The Great Waters Program must identify and assess the extent of atmospheric deposition of HAPs to the Great Lakes, Chesapeake Bay, Lake Champlain and coastal waters. The Great Waters Program must conduct atmospheric deposition monitoring, monitoring methodology research and biological sampling. In addition, the program must investigate sources and deposition rates of pollutants, investigate pollutant transformation, precursors and products, evaluate adverse effects to health and the environment, determine the relative contribution of atmospheric deposition to the total loading and assess the contribution of atmospheric deposition to water quality standards violations. In addition, Section 112(c)(6) of the CAAA requires the USEPA to list categories of sources accounting for not less than 90 percent of the emissions of alkylated lead compounds, polycylic organic matter (POMs), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), 2,3,7,8-tetrachlorodibenzo-furans (2,3,7,8-TCDF), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and mercury, and to promulgate standards for those source categories by the year 2000.

#### MICHIGAN LEGISLATIVE HISTORY

Michigan first began regulating HAPs in the late 1970s by including some HAPs in permit reviews for new sources. In 1992, specific air toxic rules were promulgated to control HAPs (known as Toxic Air Contaminants or TACs in the Michigan rule) from new or modified sources requiring air use permits to install. Michigan's air toxics rules (R336.1230 to R336.1232 also known as Rule 230) require new or modified facilities subject to the rule to limit emissions so that the ambient impact is less than the screening level for any TAC. The Michigan Air Quality Division has established screening levels for both carcinogenic and non-carcinogenic air toxics. In addition, Rule 230 requires that most sources subject to the rule install "T-BACT", which is Best Available Control Technology for Toxics. Michigan's air toxic rule regulating new or modified sources is now in effect, whereas the HAPs provisions of the CAAA, affecting both new and existing sources are being phased in over a period of time extending beyond the year 2000.

## MICHIGAN AIR TOXIC MONITORING AND INVENTORY PROGRAMS

Michigan's Hazardous Waste Management Act (Part 111 of Act 451 of 1994) and administrative rules closely regulate the disposal of hazardous waste in Michigan. Rule 409 of the administrative rules implementing Part III, requires that licensed hazardous waste disposal facilities conduct an approved air monitoring program. Under this requirement, the first facility in Michigan to monitor for VOCs and trace metals began doing so in 1985. Today, several facilities operate a Part 111 monitoring program. The parameters monitored at each facility subject to the Part 111 monitoring program vary and can include toxics such as VOCs, trace metals, dioxins, furans, hydrochloric acid and carbonyl compounds. A typical network consists of an upwind monitor to determine background concentrations and one or more monitors to measure source impact.

The Michigan Toxic Air Monitoring Program (MITAMP) was established in January 1990. Since the program's inception, 40 toxic organic compounds and 13 trace metals have been monitored at various urban locations throughout the state. High-volume sampler filters are used to collect toxic metals. PUF (Polyurethane foam) filters retain PAH's, PCB's, etc. and canisters are used to sample for VOCs.

In addition to federal and state programs, several important regional initiatives are currently underway. In 1987, the eight Great Lakes States of Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania and Wisconsin agreed to pursue the development of an automated emissions inventory system for HAPs. From this initial conceptual agreement, the Regional Air Pollutant Inventory Development System (RAPIDS) has evolved. Using RAPIDS, the Great Lakes States' air regulatory agencies are building a comprehensive computerized data management system for air toxics emissions information. RAPIDS will include specific process and emission data for point, area and mobile sources for 49 air pollutants of potential concern to the Great Lakes. By using RAPIDS, it will be possible to identify the sources and source

categories that contribute most to the total emissions in a given geographical area and to evaluate the effectiveness of different control strategies.

The Great Lakes States' Air Permitting Agreement was signed by the Great Lakes environmental administrators in November 1988. The agreement commits the air regulatory programs to require the best available control technology on sources of HAPs to the maximum degree allowed under existing authority. Special focus is placed on air emission sources of Great Lakes critical pollutants (i.e., the PHAPs) including mercury, alkylated lead compounds, total PCBs, hexachlorobiphenyl, benzo(a)pyrene (BaP), 2,3,7,8-TCDD and 2,3,7,8-TCDF. The agreement also calls for information exchange to occur among the Great Lakes States through the permitting programs.

The Lake Superior Binational program was formed in early 1995 with the goal of zero discharge of toxic pollutants to the basin. This project began monitoring efforts in late 1995 or early 1996. Attention to PHAPs became focused in 1997 with the signing of the Great Lakes Binational Toxics Strategy which will begin monitoring of 13 priority PHAPs.

Finally, with funds received through the settlement of an enforcement case, two research projects to study mercury emissions and deposition have been initiated. The first is a study of stack gases to determine the speciation of mercury from different types of sources. The states of Michigan, Wisconsin, and Minnesota have been working together with Frontier Geosciences in Seattle, Washington to conduct plume studies at three facilities. Sampling at all three sites took place in the fall of 1995. The other mercury study focuses on the transport and deposition of mercury. The funding for this study began in 1996 with an award to the University of Michigan.

### MONITORING FOR TOXICS IN MICHIGAN

Figure 4-1 shows the locations of ambient air monitoring stations that were measuring organic HAPs in Michigan in 1995. Figure 4-2 indicates the site that samples for semi-volatile organic compounds. Lastly, Figure 4-3 shows the locations that sample for trace metals. In these figures, both industrial and special study locations are shown. The legends for Figures 4-1 and 4-2 (Tables 4-1 and 4-2, respectively) list the HAPs that are measured at each station.

Of the 36 sites monitoring HAPs in Michigan, three are operated by the Michigan Department of Environmental Quality (MDEQ) to determine population exposure in high risk urban areas. The remaining sites are company-operated for the purpose of determining the maximum source impact caused by the facility on either a three-day, six-day, or 12-day monitoring frequency. Sample collection and analytical methodologies were derived from USEPA guidance documents.

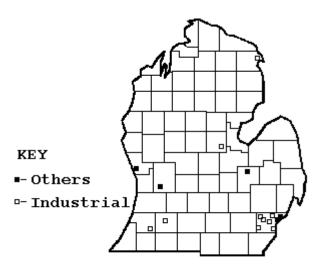


Figure 4-1. Air quality monitors for locating organic HAPs active in 1995.

Table 4-1. Figure 4-1 legend (Sampler locations and parameter code definitions).

Location	Site ID/agency & type		Parameters						
Alpena	26-007-0901 to 0903 L	aFarge Industrial		L,M,O,P,R,Y,Z,a,b,c,d,e,f,g,I,I,n,o,p,					
Alpena	20 007 0001 10 0000 2	ar argo, maastrar							
Kalamazoo	26-077-0901 to 0905 L	Iniohn Industrial	q,r,t,u,ac,ae,af,ag,ah,aj A,F,G,I,K,O,P,R,T,U,V,Y,c,d,f,g,I,m,u,v,w,z,af,ag						
Midland	26-111-0951,0953 to 0		G,N,W,Y,c,f,g,u,a						
- Wildiana	Dow, Industrial		0,11,11,11,0,1,9,4,9						
Grand	26-081-0021 MDEQ		A.B.C.D.E.F.G.H.	J,K,L,M,O,P,R,S,T,U,V,X,Y,Z,a,b,c,					
Rapids				q,r,s,t,u,x,y,z,ab,ac,ae,af,ag,ah,ai,aj					
Muskegon	26-121-0914,0915, 091	17 Lomac,	k						
	Industrial	,							
Lawton	26-159-0901 Upjohn,In	dustrial	A,F,G,I,K,O,P,R,1	۲,U,V,Y,c,d,f,g,l,m,u,v,w,z,aa,ag					
Detroit,	26-163-0005 MDEQ, C	ther	A,B,C,D,E,F,G,H,	J,K,L,M,O,P,R,S,T,U,V,X,Y,Z,a,b,c,					
River Rouge			d,e,f,g,I,I,m,n,o,p,	r,s,t,u,x,y,z,ab,ac,af,ag,ah,ai,aj					
Detroit,	26-163-0015 MDEQ, C	Other	A,B,C,D,E,F,G,H,	A,B,C,D,E,F,G,H,J,K,L,M,O,P,R,S,T,U,V,X,Y,Z,a,b,c,					
Fort Street			d,e,f,g,I,I,m,n,o,p,	g,l,l,m,n,o,p,r,s,t,u,x,y,z,ab,ac,af,ag,ah,ai,aj					
Detroit	26-163-0912 Env. Was		A,B,C,G,Y,c,d,f,I,t	u,af,ag,ah,ak					
Detroit	26-163-0920 to 0923 M	lich. Recovery	B,C,Y,c,f,I,u,af,ag,ah,ak						
	Systems, Industrial								
Detroit	26-163-0956 to 0958 D		A,c,u,af,ah						
Detroit	26-163-0960,0963,096		A,B,C,Y,c,d,f,l,u,ac,af,ag,ah,ak						
	Chem-Met Services, In								
Detroit	26-163-0975,0977,098	1 to 0983 Wayne	A,B,C,D,E,G,N,Y,c,d,e,f,g,l,u,af,ag,ah,aj						
	Disposal, Industrial								
Detroit	26-163-0996 to 0998 S	aulk Trail Hills	D,M,Q,R,Y,c,f,I,u,	af,ag,ah,aj,ak					
	Landfill, Industrial	T		T					
	Compound		pound	Symbol Compound					
A - 1,1,1 Trich		W - Acrylonitrile		t - m/p Xylene					
	trachloroethane	X - Benzaldehyde	)	u - Methylene Chloride					
C - 1,1,2 Trich		Y - Benzene		v - n-Heptane					
D - 1,1 Dichlo		Z - Benzylchloride		w - n-Hexane					
E - 1,1 Dichlo		a - Bromomethan		x - n-Butyraldehyde					
F - 1,2 Dichlor	robenzene	b - c-1,3 Dichloro	propene	y - o-Tolualdehyde					

G - 1,2 Dichloroethane	c - Carbon Tetrachloride	z - o-Xylene
H - 1,2 Dichloroethene	d - Chlorobenzene	ab - Propionaldehyde
I - 1,2,3 Triethylbenzene	e - Chloroethane	ac - Styrene
J - 1,2,4 Trichlorobenzene	f - Chloroform	ad - t-1,2 Dichloroethene
K - 1,2,4 Trimethylbenzene	g - Chloromethane	ae - t-1,3 Dichloropropene
L - 1,2 Dibromoethane	I - cis 1,2 Dichloroethene	af - Tetrachloroethene
M - 1,2 Dichloropropane	j - Crotonaldehyde	ag - Toluene
N - 1,3 Butadiene	k - Dichlorobenzidine	ah - Trichloroethene
O - 1,3 Dichlorobenzene	I - Ethylbenzene	ai - Valeraldhyde
P - 1,3,5 Trimethylbenzene	m - Formaldehyde	aj - Vinyl Chloride
Q - 1,3 Dichloropropene	n - Halocarbon 11	ak - Xylene (o,p,m)
R - 1,4 Dichlorobenzene	o - Halocarbon 113	al - 2,5 Dimethyl Benzaldehyde
S - 1 Ethyl 4 methylbenzene	p - Halocarbon 114	am - Hexanaldehyde
T - Acetaldehyde	q - Halocarbon 12	an - Iso-Valeraldehyde
U - Acetone	r - Hexachloro - 1,3 butadiene	
V - Acrolein	s - m,p Tolualdehyde	

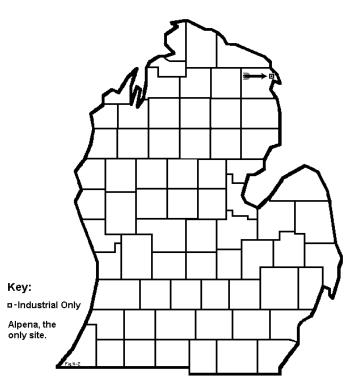


Figure 4-2. Alpena (only sampling site) air quality monitors for semi-volatile organic compounds active in 1995.

Table 4-2. Figure 4-2 legend (Sampler locations and parameter code definitions).

Location	Site ID/agency & type	!		Parameter						
Alpena	26-007-0901 to 0903	Lafarge Corp	Industrial	ABCDEFGHIJKLMNOPQRS						
Alpena	26-007-0902 Lafarge	Corp Industria	al	TUVWX	KYZabcdefghljk					
Symbol	Compound	Symbol	Compo	und	Sy	mbol Compound				
A 2-meth	yl napthalene	M Fluorant	hene		Υ	1,2,3,6,7,8-HXCDD				
B Acenna	apthalene	N Fluorene	Э		Ζ	1,2,3,6,7,8-HXCDF				
C Acena	othene	O Indeno(	123-cd)pyre	ene	а	1,2,3,7,8,9-HXCDD				
D Anthace	ene	P Napthale	ene		b 1,2,3,7,8,9-HXCDF					
E Benz(a)	anthracene	Q Perylene				c 1,2,3,7,8-PECDD				
	p)pyrene	R Phenanthrene			d 1,2,3,7,8-PECDF					
G Benzo(	b)fluoranthene	S Pyrene			e 2,3,4,6,7,8-HXCDF					
	e)pyrene	T 1,2,3,4,6	3,7,8-HPCD	D	f 2,3,4,7,8-PECDF					
I Benzo(	ghi)perylene		6,7,8-HPCD		g	2,3,7,8-TCDD				
J Benzo(	k)fluoranthene	V 1,2,3,4,	)F	h	2,3,7,8-TCDF					
K Chryser	ne	W 1,2,3,4,7,8-HXCDD				OCDD				
L Dibenzo	(ah)anthracene	X 1,2,3,4,7,8-HXCDF				j OCDF				
	·	-								

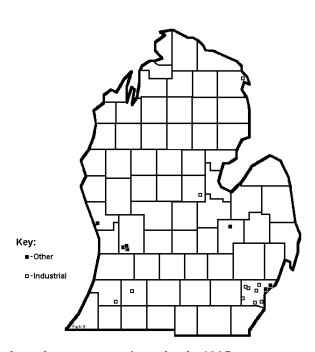


Figure 4-3. Air quality monitors for trace metals active in 1995.

Table 4-3. Figure 4-3 legend (sampler locations and parameter code definitions).

Location	Site ID/agency and company	Parameters
Alpena	26-007-0901 to 0903	Sb, As, Ba, Be, Cd, Cr, Pb, Ni, Ag, Ti, V, Zn
	LaFarge Corp, Industrial	
Flint	26-049-0021 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Kalamazoo	26-077-0905 Upjohn, Industrial	Cd, Cr, Cu, Pb, Zn
Grand Rapids	26-081-0010 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Grand Rapids	26-081-0021 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Wyoming	26-081-2002 MDEQ	Be, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Midland	26-111-0951, 0953 to 0955 Dow	As, Cd, Cr
	Chemical, Industrial	
Muskegon	26-121-0023 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Lawton	26-159-0901 Upjohn, Industrial	CD, Cr, Cu, Pb, Zn
River Rouge	26-163-0005 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Detroit	26-163-0015 MDEQ	Be, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn
Detroit	26-163-0920 to 0923 Michigan	CD, Pb
	Recovery Systems, Industrial	
Detroit	26-163-0925 to 0928 Huron Ash	As, Cd, Cr, Pb, Hg, Ni
	Monofill, Industrial	
Detroit	26-163-0935 to 0937 Dynecol Inc.,	As, Cd, Cr, Cu, Pb, Ni, Zn
Detroit	26-163-0960, 0963, 0965, 0967,	Cd, Cr, Cu, Pb, Zn
	Chem-Met Services, Industrial	
Detroit	26-163-0975, 0977, 0981 to 0983	Cd, Cr, Cu, Pb, Zn
	Wayne Disposal Inc. Industrial	
Detroit	26-163-0994, 0995 Carleton	Cd, Pb, Hg
	Farms, Industrial	
Detroit	26-163-0996 to 0998 Saulk Trail	Cd, Cr, Pb
	Landfill, Industrial	

#### ASSESSING THE AMBIENT DATA

The Task Force attempted to asses the existing ambient air quality database with the assistance of the MDEQ staff. During the assessment, the MDEQ discovered numerous errors in the data set. While the MDEQ believes much of the monitoring data collected is valid, at this point the extent of the errors is not clear. However, given the existence of the errors and the absence of a simple correction, the Task Force has reached the conclusion that the uncertainties associated with the database preclude an assessment of the relative risk posed by exposure to these hazardous air pollutants in Michigan.

## CONCLUSIONS AND RECOMMENDATIONS

The chemicals defined in the chapter as HAPs are potential public health concerns and include the 188 compounds identified in the 1990 CAAA and the over 750 compounds for which screening levels have been developed under the Michigan air toxic rules. Due to the CAAA and the MDEQ air toxic program, major sources of HAPs have been identified and subjected to federal and state regulations. However, because of errors in the ambient air monitoring database, an assessment of the relative risk associated with the HAPs is not possible. The Task Force recommends that the MDEQ makes it a high priority to determine what data from the existing monitoring database is correct and of high quality and to collect additional high quality ambient air HAPs so that such an assessment can be conducted in the near future. The Task Force further recommends that the existing federal and state programs to reduce HAPs be continued while the ambient air assessment is being conducted.

### CHAPTER 5. PERSISTENT HAZARDOUS AIR POLLUTANTS

The air quality issue that was the highest ranked environmental issue of concern in the 1992 Michigan Environmental Relative Risk Analysis project (Rustem *et al.*, 1992a) was "atmospheric transport and deposition of air toxics." Although this issue considered all of the hazardous air pollutants (HAPs) discussed in the previous chapter, the high ranking was due to a relatively small number of persistent hazardous air pollutants (PHAPs). The PHAPs will be considered as a separate issue in this chapter.

The persistence of PHAPs allows them to be transported long distances, to remain in the environment for a significant period of time, and to accumulate over time. The ability of some of these pollutants to bioaccumulate and biomagnify results in chemical concentrations in top predatory species that are several orders of magnitude greater than that in natural waters or in the lower levels of the food chain.

The Great Lakes Water Quality Agreement, of which the U.S. is a signatory, requires the input of PHAPs to the Great Lakes basin ecosystem to be virtually eliminated. In a 1994 report of the International Joint Commission (IJC, 1994), the conclusion was drawn that:

"Mounting evidence continues to reinforce concerns about the effects of persistent toxic substances. Long-term exposure to these substances has been linked to reproductive, metabolic, neurological and behavioral abnormalities; to immunity suppression leading to susceptibility to infections and other life-threatening problems; and to increasing levels of cancers."

The first Great Waters Report to Congress (USEPA, 1994a) also made some important conclusions as a result of recent findings in the scientific literature. These findings are as follows:

"Persistence and the tendency to bioaccumulate are critical characteristics of the pollutants of concern, and cause potentially greater exposure of a pollutant to the environment. Furthermore, as a result of these characteristics, water quality criteria and standards for some pollutants have been exceeded in the past. Often considered to be unrelated, the human and wildlife effects of these chemicals are essentially linked. As the USEPA's Science Advisory Board pointed out, "most human activities that pose significant ecological risks pose direct or indirect human health risks as well."

"Atmospheric deposition is a major contributor of mercury, polycyclic organic matter (POMs) and polychlorinated biphenyls (PCBs). Attention should be given to the absolute quantity of the loadings because even small amounts of the pollutants that bioaccumulate can produce a burden in fish, and ultimately, in humans."

"Significant adverse effects on wildlife have been observed due to exposure to persistent pollutants that bioaccumulate. These adverse effects range from immune system disease and reproductive problems in wildlife to subtle developmental and neurological impacts on fetuses and young."

"In addition to their persistence, several of the PHAPs undergo atmospheric reactions transforming them into compounds more mutagenic, and potentially carcinogenic than when in their original form. Recent research also suggests that these compounds can act in a synergistic manner to cause endocrine disruption (Arnold *et al.*, 1996)."

## STANDARDS/REGULATIONS/AGREEMENTS

In the 1970's Michigan began regulating toxic air pollutants by including them in the permit review process for new sources (MDEQ, 1994). These rules were refined to control toxic air pollutants from all new sources, including existing sources where modifications to the source were made and for which an air permit is required.

The 1986 Great Lakes Governors' Toxic Substance Control Agreement specified provisions to address atmospheric deposition with a commitment to cooperate in quantifying the loadings of toxic substances originating from all sources, with the purpose of developing the most environmentally and economically sound control programs. In 1987, in response to the Governors' lead, the state air programs began the development of a computerized air toxics database. This Great Lakes states database was initiated for the purpose of obtaining a better understanding of the nature and sources of toxic air emissions and their migration, dispersion, and resulting impact upon the Great Lakes basin.

The 1990 Clean Air Act Amendments (CAAA) identified 189 compounds as HAPs and brought these pollutants into a special focus by formulating an aggressive strategy to limit the burden of these pollutants in the environment. Section 112 of the CAAA details the legislative basis for the USEPA hazardous pollutant programs. With mounting evidence that air pollution contributes to surface water pollution, Congress included section 112(m) Atmospheric Deposition to Great Lakes and Coastal Waters, referred to as the Great Waters Program, to establish research and reporting requirements related to atmospheric deposition of HAPs to the Great Waters.

Among the HAPs listed currently in the CAAA, 40 percent have had no atmospheric measurements made and another 20 percent have very little monitoring data. For a few compounds, there are considerable monitoring data collected at a variety of locations to assist with exposure assessment. For many of the PHAPs, indirect rather than direct exposure is of the most concern. For these compounds, a quantitative assessment must be made of the relative contribution of atmospheric deposition to water column concentrations and ultimately to ingested levels of the persistent bioaccumulative HAPs. In an industrial/urban area, assessment of the atmospheric component to levels in the food chain is not an easy task. In areas remote from direct

discharges, it is evident that deposition of very small amounts of PHAPs from the atmosphere can result in pollutant levels in fish that are above currently accepted safe levels for fish consumption.

Currently, there are health effects data available for each of the 189 HAPs. However, in many cases there are little data available regarding all of the endpoints of concern including cancer, developmental and reproductive effects, neurotoxicity, and short-term and long-term pulmonary effects. Mercury is a notable exception. As a result of the Minamata Bay disaster in the 1950's, and more recent studies in native populations in Canada and the United States, much has been learned about health effects due to environmental mercury exposure. Also, as a result of congressional focus on mercury in the 1990 CAAA, much is being learned about the sources and cycling of mercury.

The cancer and non-cancer risks for a number of PHAPs are listed in Table 5-1 along with reference air concentrations and reference doses where available. Reference air concentrations and references doses are established by the USEPA as the concentration which, over a lifetime of exposure, would not likely result in noncancer effects.

Table 5-1. Persistent HAPs and their carcinogenicity potential, noncancer effects, reference concentrations and reference doses.

PHAP	Cancer	Noncancer Effects	Reference Concentration µg/m³	Reference Dose mg/kg/day
Cadmium Compounds	Probable	R,N,I,O	not established	0.001
Chlordane	Probable	R,N,I,E,O	under review	0.00006
DDT/DDE	Probable	R,N,I,O	not established	not established
Dieldrin	Probable	R,N,I,E,O	not available	not available
Hexachlorobenzene	Probable	R,N,I,E,O	inadequate data	0.0008
α-HCH	Probable	0	under review	0.0003
Lindane	Probable	R,N,I,O	under review	0.0003
Lead Compounds	Probable	R,N,I,E,O	not established	not established
Mercury Compounds		R,N,I,E,O	0.3(elemental Hg)	0.0003 (methyl Hg)
PCBs	Probable	R,N,I,E,O	not established	0.00007*
POM	Probable	R,I,O	not established	not established
2,3,7,8-TCDF	Not classifiable	R,I,E,O	under review	not established
2,3,7,8-TCDD	Probable	R,N,I,E,O	not established	not established
Toxaphene	Probable	R,N,I,E,O	not established	not established

Noncancer Effects: R=Reproductive Effects, N=Neurological/Behavioral effects, I=Immunological Effects, E=Endocrine Effects, O=Organ Toxicity (lung, kidney, liver, blood cells).

Clearly, few reference concentrations exist for PHAPs due to limited monitoring data and slowly developing toxicity tests which can adequately screen the large number of potential toxins currently being emitted from anthropogenic sources in Michigan. Reference values that do exist, as well as cancer risk estimates are likely to change as new and better screening methods become available. In general, people are exposed

<sup>\*</sup>For Aroclor 1016, USEPA 1994

to mixtures of many pollutants simultaneously, and how these mixtures affect human health is only poorly understood.

#### FOCUS POLLUTANTS

There are 189 chemicals and chemical compounds listed as HAPs in the 1990 CAAA. Among those, the PHAPs, some of which are still being identified, are of special interest due to their ability to cause cancer and non-cancer effects in humans and wildlife populations in Michigan. The HAPs which have been identified by the USEPA as bioaccumulative chemicals of concern are listed in Table 5-2. Additional potentially bioaccumulative chemicals of concern identified by the USEPA are listed in Table 5-3.

Table 5-2. Bioaccumulative chemicals of concern for the Great Lakes (a).

Aldrin	4-Bromophenyl phenyl ether
Chlordane	DDD, DDE, DDT
Dieldrin	Heptachlor; Heptachlor epoxide
Endrin	Hexachlorobutadiene; hexachloro-1,3-butadiene
Hexachlorobenzene	Hexachlorocyclohexane (and its $\alpha$ , $\beta$ , $\delta$ , and $\gamma$ isomers)
Mercury	Lindane (γ-hexachlorohexane)
Methoxychlor	Polychlorinated biphenyls
Mirex; dechlorane	Pentachlorobenzene
Octachlorostyrene	2,3,7,8-TCDD; dioxin
Toxaphene	1,2,3,4-Tetrachlorobenzene
Photomirex	1,2,4,5-Tetrachlorobenzene

(a) USEPA, 1994.

Table 5-3. Potential bioaccumulative chemicals of concern for the Great Lakes(a).

Benzo(a)pyrene; 3,4-benzopyrene	3,4-Benzofluoranthene; benzo(b)fluoranthene
4-Chlorophenyl phenyl ether	11,12-Benzofluoranthene; benzo(k)fluoranthene
Dibutyl phthalate; di-n-butyl phthalate	1,12-Benzoperylene; benzo(ghi)perylene
Phenol	1,2:5,6-Dibenzanthracene; dibenz(a,h)anthracene
Toluene; methylbenzene	Ideno(1,2,3-cd)pyrene; 2,3-o-phenylene pyrene

(a) USEPA, 1994.

Not all of these compounds have adequate information on levels or emissions to warrant their inclusion in this chapter. This chapter will focus on the selected pollutants of concern for the Great Waters Program and those which have been selected for attention in the 1997 Great Lakes Binational Toxics Strategy Agreement. This group of 14 chemicals or chemical compounds was selected because they are all on the 1990 CAAA HAPs list and they are pollutants that persist in the environment, can cause adverse effects in humans and in the environment, and/or have a high potential to accumulate in living organisms.

All of the pollutants have been measured in the Great Waters Program and are known to be introduced to the Great Waters region via atmospheric deposition. The persistent pollutants include mercury, PCBs, pesticides, and POMs. The list of pollutants is given

in Table 5-4 and is discussed by compound class (metals, organochlorines, and POM's in a later section of this report.

Table 5-4. Persistent HAPs in the Great Lakes Binational Toxics Strategy.

Aldrin/dieldrin	Hexachlorobenzene (HCB)
Benzo(a)pyrene	Mercury and mercury compounds
Chlordane	Octachlorostyrene
DDT/DDE	Polychlorinated biphenyls (PCBs)
Alkyl-lead	Tetrachlorodibenzo-p-dioxin, 2,3,7,8- (2,3,7,8-TCDD; dioxins)
Mirex	Tetrachlorodibenzofuran, 2,3,7,8- (2,3,7,8-TCDF; furans)
Toxaphene	

### MICHIGAN AIR TOXICS PROGRAMS

Figure 5-1 identifies the locations across the state where reliable data exist for the compounds being discussed. There are currently only two sites at which the routine monitoring of a large number of HAPs are performed and these are part of the Integrated Atmospheric Deposition Network (IADN). In addition, the sites where measurements were being made from 1992-1994 in Michigan are shown in Figure 5-2. During the summer of 1991 a cooperative research effort between the USEPA Atmospheric Exposure Assessment Laboratories and the University of Michigan, Lake Michigan Urban Air Toxics Study (LMUATS), was conducted which assessed the levels of many of the PHAPs of interest. Many high quality measurements made in the state were performed under special research programs funded by the USEPA in cooperation with the states as part of the Lake Michigan Mass Balance Study. Two Michigan Toxic Air Monitoring Program (MITAMP) sites (Monosmith, 1995) were in operation in the Detroit area with a third site scheduled to be operated in 1995.

The levels of HAPs in Michigan have only recently been studied in a systematic manner as part of a cooperative research study (Keeler *et al.*, 1997). The overall goal of this project, referred to as MTOX, was to conduct a two-year study to investigate the levels, transport, and sources of toxic contaminants measured across Michigan. The specific objectives of the project were to (1) determine the concentration of specific PHAPs in the atmosphere, (2) investigate the seasonal variation of the PHAPs in Michigan, (3) assess the spatial gradient in atmospheric levels in Michigan and (4) evaluate the atmospheric transport of these species across Michigan. The results of this as well as other studies conducted in Michigan are summarized here to provide an indication of the levels in rural and urban areas of the state.

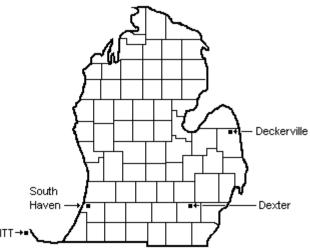


Figure 5-1. PHAP measurement sites (LMUATS and MTOX).

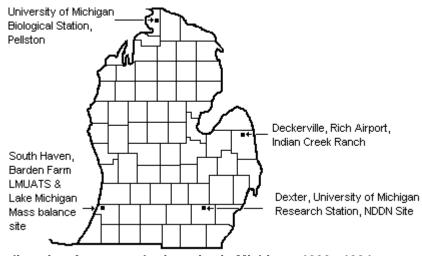


Figure 5-2. Sampling sites for atmospheric toxics in Michigan, 1992 - 1994.

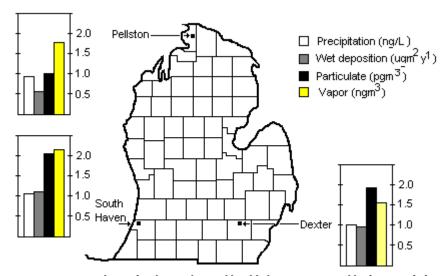


Figure 5-3. Average vapor and particulate-phase Hg. Vol-wt average Hg in precipitation and year average Hg wet deposition at three sites in Michigan.

## **MERCURY**

As progress has been made in recent years in understanding the cycling of mercury (Hg) in aquatic and terrestrial ecosystems, the importance of the atmospheric pathway to these cycles has become well recognized (Lindqvist, 1991). It is believed that even modest increases in atmospheric Hg loadings could lead directly to elevated levels in the fish stock. The extent to which anthropogenic emissions of mercury affect levels in lakes and ultimately fish, is one of the primary focuses of the "Mercury Report to Congress" prepared by the USEPA. The report was finalized in December 1997 (USEPA, 1997).

Anthropogenic emissions (both primary emissions and resuspended deposited material) have been recognized as the dominant contributing factor to the total atmospheric Hg burden (exceeding the contribution from natural sources) (EPRI, 1994). Since combustion and manufacturing operators are not yet required to measure Hg emissions, information regarding the relative contribution of each of the anthropogenic source types to total atmospheric Hg is not available.

# Mercury Measurements in Rural Michigan Locations

Atmospheric mercury measurements were initiated in Michigan in 1992 to assess the sources contributing to the atmospheric deposition of Hg in Michigan (Keeler and Hoyer, 1997). Two years of Hg measurements in precipitation were made and one year of vapor- and particle-phase Hg was collected at Pellston, South Haven and Dexter, Michigan. The yearly average concentrations of aerosol-associated Hg, Hg in precipitation and Hg wet deposition were significantly higher at the southern Michigan sites than in northern Michigan (p<0.0001, Kruskal-Wallis method) (Figure 5-3). The average vapor-phase mercury concentration at South Haven, in southwestern Michigan, was significantly higher than that at Pellston (p<0.002, Kruskal-Wallis method).

Significant seasonal variation was observed for particulate Hg concentrations and Hg in precipitation. Similar transport conditions and source influences were identified for the majority of precipitation events in Michigan which had high Hg concentrations. Wet deposition of Hg during the spring and summer comprised 66 - 71 percent of the total Hg wet deposition, while the wet deposition in winter comprised only nine to 11 percent of the total Hg wet deposition. The seasonal variation in Hg wet deposition may have important ecological consequences, including enhanced uptake by aquatic organisms since the majority of Hg delivered to the surface via precipitation occurred during the growing season when biological activity and productivity are at their highest levels.

While the rural concentrations of Hg measured in Michigan decrease with distance from the major anthropogenic sources, mass balance estimates (Fitzgerald *et al.*, 1991) and Hg-laden fish in remote lakes (Hg >0.5 ppm) suggest that Hg deposition equal to or lower than that measured in Pellston, Michigan can account for the Hg measured in fish tissue in most inland lakes.

# Mercury Measurements in Detroit

Ambient air concentrations of particulate mercury and a suite of other trace metals (Fe, Zn, Pb, Ni, Cr, Cd, Be) have been measured since the early 1980's at seven urban sites across the city of Detroit (Pirrone *et al.*, 1995). An analysis of the Hg data from 1986-1992 revealed a 16 percent increase in the atmospheric concentrations of particulate Hg. This increase was accounted for by an 11 percent increase in the quantity of wastes incinerated in the city and a five percent annual increase in Hg emissions from other sources (Pirrone *et al.*, 1996). More recently, the University of Michigan Air Quality Laboratory (UMAQL) has made measurements of ambient mercury as well as Hg in urban runoff and in both wet and dry deposition. Ambient levels of Hg tend to be two to three times higher in the urban Detroit area over those measured in more rural areas. Levels of Hg deposition across the state have not varied over the many years that the UMAQL has been making measurements.

### ORGANOCHLORINE COMPOUNDS

The organochlorine compounds include pesticides, and combustion emissions of PHAPs. Persistent pesticides of particular concern in Michigan include atrazine, chlordane, DDT/DDE, dieldrin,  $\alpha$ -HCH, HCB (and other chlorinated benzene compounds), hexachlorobutadiene, lindane, methoxychlor, mirex and toxaphene. Although the use of pesticides is significantly restricted, it continues to be a concern to inland lakes and the Great Lakes because of their persistence.

The PHAPs emitted during combustion include PCBs, 2,3,7,8-TCDD and 2,3,7,8-TCDF, octachlorostyrene and POM (the latter of which is discussed below). These pollutants are released to the atmosphere during combustion of fossil fuels and/or during manufacturing or incineration processes.

Several of the chlorinated compounds of concern in Michigan were analyzed during the MTOX study and the percent of samples with values above detection limits (typically <0.001 ng/m³) for these compounds are listed in Table 5-5.

DDT was manufactured to control insects on agricultural crops and insects that carry diseases. The degradation products of DDT include DDE and DDD, the most common of which is DDE. Although DDT was banned by the USEPA in 1972, use of pesticides contaminated with DDT was not. During the LMUATS and MTOX studies, exceptionally elevated DDT concentrations were observed in southwestern Michigan. The average total DDT concentration measured over the two-year period from 1992 - 1994 at South Haven was 952 pg/m³, which is over 20 times higher than concentrations observed at the other sites in Michigan (Table 5-6).

Table 5-5. The percent of samples with values above the detection limit for chlorinated organic compounds at four rural sites in Michigan in 1992-1994.

Compound	South Have	n	Dexter		Deckerville				
	n=84		n=96		n=64		n=84		
	Particulate	Vapor	Particulate	Vapor	Particulate	Vapor	Particulate	Vapor	
α-HCH	40	99	15	100	17	95	5	100	
γ-HCH (Lindane)	17	99	14	100	30	98	21	100	
Dieldrin	49	95	76	99	67	95	58	98	
Dicofol	4	43	28	54	16	50	18	44	
p,p'-DDE	76	100	100	98	73	97	85	96	
p,p'-DDD	13	51	41	80	11	64	12	50	
p,p'-DDT	62	93	92	100	69	94	55	96	
1245	15	51	10	56	11	55	5	50	
Tetrachlorobenzene									
1234	27	54	16	58	17	56	17	54	
Tetrachlorobenzene									
Pentachlorobenzene	52	54	46	58	48	56	45	54	
Hexachlorobenzene	90	99	82	99	84	98	81	100	
Octachlorostyrene	23	50	21	51	30	45	23	54	
Total PCB	98	99	99	99	97	98	96	100	

Dichlorodiphenyltrichloroethane (DDT)

The total DDT concentrations measured at this location in southwestern Michigan are an order of magnitude higher than typical levels reported for other rural locations in the region (Kelly *et al.*, 1991; Bidleman *et al.*, 1992; Reid, 1992; Hoff *et al.*, 1992). The recent finding of elevated DDT appears to be restricted to southwestern Michigan, strongly suggesting an important local source for this toxin. This finding is an important indicator of the potential for rural hotspots to contribute a substantial load of these toxins to waterways in the region.

Table 5-6. Average summer concentrations of DDT, DDD and DDE at three Lake Michigan Urban Air Toxics Study sites and four rural Michigan sites (units = pg/m³).

	LMUATS Sites	1		Michigan Sites							
agent	Kankakee	IIT	South Haven	South Haven	Pellston	Deckerville	Dexter				
	n=15	n=16	n=21	n=96	n=84	n=64	n=84				
DDT	0.01±0.02	0.18±0.13	0.34±0.17	0.26± 0.38	0.01 ±0.008	0.01±0.01	0.02±0.01				
DDD	0.003±0.01	0.004±0.01	0.01±0.01	0.01±0.01	0.002±0.002	0.002±0.003	0.003±0.01				
DDE	0.04±0.03	0.12±0.10	1.3±0.35	0.69±1.1	0.01±0.01	0.01±0.02	0.03±0.03				
Total DDT*	0.05±0.05	0.31±0.24	1.7±0.52	0.95± 1.5	0.02±0.01	0.02±0.03	0.05±0.04				
DDT:DDE	0.3±0.3	1.5±1.1	0.3±0.3	0.5±0.4	NA	NA	0.8±0.3				

\*Total DDT is the sum of DDT, DDD, and DDE (all p,p'- congeners)

NA - DDT:DDE ratios were not applied to Pellston and Deckerville as concentrations were near the detection limit.

Since DDT degrades to form DDE, the ratio of DDT to DDE has been used to indicate whether DDT measured is due to a recent or an old application of the material. A high DDT:DDE ratio (>1.0) indicates that DDT was recently applied, whereas a low DDT:DDE ratio (<1.0) indicates that the DDT levels are due to a previous application. Current DDT:DDE ratios in air from the Great Lakes region are typically less than 1.0 (Table 5-6) suggesting that previously applied DDT is primarily contributing to the atmospheric levels observed. At IIT, the DDT:DDE ratio of 1.5 is suspected to be the result of the recent use of DDT-containing pesticides used to control cockroaches and other household pests. DDT:DDE ratios were not applied to Pellston and Deckerville data since concentrations at these sites were often near the detection limit.

# CHLOROBENZENE COMPOUNDS

Chlorobenzenes (CBs) are a group of 11 isomers ranging from monoto hexachlorinated. Unlike some organic compounds, including PCBs and various pesticides, CBs are not banned from production or use in any country. They are often synthetic precursors, by-products, or contaminants resulting from synthesis or degradation of other organic compounds. They cover a wide range of volatility, some with vapor pressures comparable to various pesticides (Lane *et al.*, 1992). Background concentrations of individual CBs may be greater than total PCBs (Atlas and Giam, 1989). Evaporation of CBs from soil amended with sewage sludge (Wang *et al.*, 1995) or from water surfaces contaminated with waste CBs (Oliver, 1987) are two known, significant mechanisms of CB transfer to the atmosphere. CB inputs to the atmosphere are likely to be considerable, but also variable, depending upon industrial activities, discharges, and land applications.

Hexachlorobenzene (HCB) has been classified as a probable human carcinogen (Newhook and Meek, 1994) and is known to have a high bioaccumulative potential (Williams *et al.*, 1988). Due to the shorter half-lives of the other CB isomers, and the fact that they have not been classified regarding the potential to cause human cancer, these isomers have seldom been collected and analyzed (Gidding *et al.*, 1994a; 1994b). Nevertheless, because other CBs have been observed in birds and fish their occurrence warrants attention and they have now been listed as contaminants of concern (Gebauer and Weeseloh, 1993; Oliver, 1987; Renner, 1995; Final Water Quality Guidelines, 1995). CBs analyzed for the MTOX study included 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), pentachlorobenzene (PeCB) and HCB which are reported in Table 5-7.

The concentrations of HCB measured at the rural sites in Michigan are similar to those reported by Monosmith and Hermanson (1996) who observed a range in HCB concentrations from 0.04-0.18 ng/m³ at three rural locations in Michigan, and Cohen *et al.* (1995) who reported annual averages of 0.06-0.10 ng/m³ at two rural locations in Michigan.

Table 5-7. Average, standard deviation and maximum vapor phase concentrations (ng/m³) for the chlorinated benzene compounds at four rural sites in Michigan, 1992-1994.

agent	evaluation	Deckerville	Dexter	South Haven	Pellston
1,2,3,4-	Avg (StdDev)	0.06 (0.02)	0.06 (0.04)	0.05 (0.02)	0.05 (0.03)
TeCB	Max (Date)	0.11 (10/22/93)	0.23 (6/12/93)	0.13 (12/15/93)	0.16 (8/23/93)
1,2,4,5-	Avg (StdDev)	0.03 (0.01)	0.041 (0.06)	0.03 (0.01)	0.03 (0.02)
TeCB	Max (Date)	0.06 (10/16/93)	0.36 (6/24/93)	0.09 (6/24/93)	0.13 (6/24/93)
PeCB	Avg (StdDev)	0.09 (0.11)	0.07 (0.04)	0.10 (0.16)	0.04 (0.02)
	Max (Date)	0.66 (12/3/93)	0.18 (6/24/93)	0.86 (6/12/93)	0.11 (6/24/93)
HCB	Avg (StdDev)	0.09 (0.03)	0.09 (0.03)	0.08 (0.03)	0.07 (0.02)
	Max (Date)	0.16 (7/6/93)	0.18 (6/24/93)	0.20 (7/24/93)	0.14 (6/24/93)

#### POLYCHLORINATED BIPHENYLS

PCBs are a chemically manufactured mixture of 209 congeners, of varying physical, chemical and toxicological properties, (Hutzinger *et al., 1974;* Lake Superior LaMP, 1996). Since the 1930's, fluids containing PCBs were used extensively in electrical, hydraulic and other equipment. In 1979, the manufacture of PCBs was banned; yet, because of their resistance to degradation, and the continued use, storage and disposal of PCB contaminated equipment, these toxic compounds persist in the environment today and will likely remain for decades to come.

PCBs are widely dispersed in the environment and bioaccumulate in the food chain. Predatory species, higher in the food chain, have been shown to be at particular risk from exposure to PCBs (D'Itri and Kamrin, 1983). PCBs have been linked to causing developmental and reproductive problems and they are a probable carcinogen (Lake Superior LaMP, 1996; USEPA, 1994a). Recently, Jacobson and Jacobson (1996) found that *in utero* exposure to PCBs affects intellectual ability, short and long term memory and focused and sustained attention in school-age children.

Despite the fact that PCBs have been banned for nearly 20 years, recent studies have shown that atmospheric concentrations have not decreased (Panshin and Hites, 1994). Cycles of volatilization and adsorption of PCBs between environmental compartments occurs and is dependent upon concentration, temperature, meteorology, hydrology and other factors (Achman *et al.*, 1993; Hornbuckle *et al.*, 1995; Hornbuckle *et al.*, 1994; Baker and Eisenreich, 1990). The Great Lakes, with their large surface areas, long residence times, and proximity to large industrial sources are extremely susceptible to atmospheric deposition of PCBs. Recently, Baker *et al.* (1992) determined that the atmosphere is responsible for approximately 77 - 89 percent of the PCB loading to Lake Superior.

PCBs exist in the atmosphere in two phases-gas and particulate. Phase distributions are dependent on the vapor pressure of the congener, the ambient temperature and the concentration, size and composition of atmospheric particulate matter (Baker *et al.*, 1992). In this study, both the particulate and gas phases of the individual PCB congeners were sampled and analyzed. Because the vapor phase was predominant in

most samples, discussion here will focus primarily on the vapor phase concentrations. A total of 26 PCB congeners represented by 15 gas chromatograph peaks were selected for detailed consideration. These congeners of interest (COI) had the highest concentrations among the PCB's detected and have also been the focus of other studies investigating atmospheric PCB levels (Monosmith and Hermanson, 1996). These COI are significant in aquatic biota and sediments (Muir *et al.*, 1988).

# Event-to-Event and Seasonal Variation in PCB Concentrations

Total vapor phase PCB concentrations measured during the study ranged from 15 pg/m³ at Pellston to 1189 pg/m³ at South Haven. Maximum vapor phase concentrations observed at each site occurred at different times and varied in magnitude. Maximums were: Deckerville- 459 pg/m³ on July 11, 1992, Dexter- 622 pg/m³ on October 15, 1992, Pellston- 313 pg/m³ on July 17, 1992 and South Haven- 1189 pg/m³ on June 6, 1993.

In contrast, the maximum total particulate phase PCB concentrations at each site were less diverse and all of them occurred in 1992. Maximum concentrations were: Deckerville- 83 pg/m³ on November 26, 1992, Dexter- 75 on June 29, 1992, Pellston-99 pg/m³ on June 29, 1992 and South Haven- 75 pg/m³ on June 17, 1992. Pellston, the northernmost site, had the lowest maximum vapor phase total PCB concentration, and the highest maximum particulate phase concentration of all the sites. At South Haven, the southernmost site of the study, the opposite was true.

# <u>Site Comparisons: Vapor Phase Concentrations</u>

The PCB data collected in the two-year study indicate that the sites were more dissimilar than similar with respect to these compounds. Of the investigations undertaken with the data thus far, no distinct similarities have emerged between any of the sites, aside from the well documented seasonal variation phenomena. Higher seasonal averages of the total PCBs and COI occurred at different times at all of the sites. At Deckerville, unusually high concentrations not seen at the other sites occurred in fall 1993, at Pellston they occurred in spring 1992, and at Dexter in fall 1992. Annual averages for total vapor phase PCBs and most of the COI were highest in 1992 at Pellston, Deckerville and Dexter. South Haven concentrations of vapor phase total PCBs and COI rose sharply in 1993, making the annual averages higher there in 1993 rather than 1992. The Deckerville site had comparable total PCB and COI summer 1992 averages to the Dexter and South Haven sites; but in 1993, for all but PCB 52, the summer averages there were lower than Dexter and South Haven by at least 25 - 50 percent.

Overall, the highest seasonal averages and individual sample concentration peaks occurred at South Haven, but, in 1992 many of the COI and total PCB seasonal averages at the Dexter site exceeded those at South Haven. As stated previously, broad comparisons using averages calculated annually or over the entire study cannot be made because of the lower amount of non-summertime samples collected at the

Dexter site. However, the statement can be made that the southern Michigan sites of Dexter and South Haven had higher average concentrations of total PCBs and of most of the COI than the northern sites of Deckerville and Pellston. Pellston had the lowest concentrations of the four sites, average concentrations during both summer seasons at Pellston were 1.5 times less than Deckerville and two times less than South Haven. It was a rare occurrence when the Pellston site had individual sample concentrations of vapor phase total PCB or COI that exceeded concentrations measured at the other sites.

At times, an individual congener exhibited a stronger influence at one site than it did at the others. In the fall 1993, concentrations of vapor phase PCB 153+132+105 were high at the Pellston site and not anywhere else. PCB 18+15 averaged higher at the Dexter site in the fall 1992. Undoubtedly, the most puzzling observations of this study were the elevated concentrations of PCB 52 noted at all sites in 1993, but most striking at Deckerville. At this time, it is unknown by what this was caused. These spatial and temporal effects of different congeners, most likely indicate impact to the site from different source regions.

Standard deviations were calculated for the weight percents of COI at the sites and are shown in Table 5-8. These standard deviations show several things. First of all, for many of the COI at all of the sites, percents were very consistent from season to season, and they did not vary much throughout the entire two year study. For PCB 8+5 and PCB 31+28, the weight percent of total PCB did not vary much at the Deckerville or Dexter sites from season to season, and it was always higher than PCB 31+28. Pellston and especially South Haven, show a much greater variance than the other two sites for these volatile congeners. Hornbuckle et al. (1995) concluded that volatilization of PCBs from Lake Michigan, especially of the tri- and tetrachlorinated biphenyls are a major source to the regional atmosphere. The South Haven and Pellston sites are closer in proximity to Lake Michigan than the other two sites and may have been influenced by volatilization from the Lake. Hornbuckle et al.(1995) did not include data on the dichlorobiphenyls, but it appears that they may also be a major component of the mix of PCB congeners that volatilize from Lake Michigan. Pellston had the highest percent of PCB 8+5 in winter 1994, which was probably due to the extremely cold temperatures. South Haven had the highest percent of PCB 8+5 in summer 1993 making it more likely due to volatilization or possible transport from the industrialized area in the southern Lake Michigan basin.

### POLYCYCLIC ORGANIC MATTER

POMs comprise a large group of compounds including volatile, semi-volatile and particulate species. These have only recently been quantified individually in atmospheric samples. The most commonly measured POM is benzo(a)pyrene which is

Table 5-8. Standard deviations of the weight percents of congeners.

Table 5-6. Standar	_									_							T.	1	-	T=
PCB Concentrations	pg/m³	8	18	31	33	47	49	52	56	70	77	95	101	153	163	187	ΣPCB	∑PCB	Ref	Description
<b>Great Lakes Region</b>		5	15	28		48			60	76	110			132	138	182	vapor	particulate		
														105						
Deckerville, MI	1992-1994	20	7	15	7	3	3	10	7	6	4	4	4	3	2	1	182	14	This	∑PCB=121 congeners
Dexter, MI	1992-1994	28	10	22	9	4	4	8	9	8	6	6	6	5	3	2	244	11	study	
Pellston, MI	1992-1994	12	4	10	4	2	2	5	4	4	3	3	3	3	2	1	111	13		
South Haven, MI	1992-1994	30	9	21	8	4	4	8	8	8	6	5	5	4	2	1	236	18		
Bay Port, MI (Saginaw)	1990-1991	61	18	39	23	9		17	14	13	11	12	9	8	4	3	469	8		∑PCB=121 congeners
Sault Ste. Marie, MI	1990-1991	29	8	20	8	4		7	6	6	6	6	5	4	2	2	198	4		
Traverse City, MI	1990-1991	72	28	62	21	7		24	8	18	21	19	20	12	7	3	616	7		
Point Petre, ON	1990-1993		10					7					3				170	5		
Eagle Harbor, MI	1993	10	4	13	4	2	3	5	4	5		4	4	8	3		128	5		
Sturgeon Pt., NY	1993	38	15	33	13	6	8	17	8			14	11	10	4		356	9		
Sleeping Bear Dunes, MI	1993	17	7	19	6	4	4	7	5	7		6	5	8	3		183	6		
Bloomington, IN	1986-1988																1700-3800 (sum)	40		∑PCB=61 congeners
																	270-580 (wint)			
Bloomington, IN	1993 (Apr-Jun)																650-2530			
Lake Superior*	1986 (Aug)		75	224	47	20	25		18		57		15				1250			∑PCB=35 congeners
Lake Michigan*	1991-1992																514			
N. Green Bay, WI*	1989 (Jun-Oct)		19	46		10	9		8	15	6		9	8	4	2	328			∑PCB=85 congeners
Central Green Bay, WI*	1989 (Jun-Oct)		19	51		12	12		10	17	8		11	7	5	1	395			
S. Green Bay, WI*	1989 (Jun-Oct)		78	199		38	40		35	47	19		20	15	8	3	1206			
Univ of WI-Green Bay	1989 (Jun-Oct)		22	46		8	8		8	13	6		10	9	5	3	338			
Peninsula St Park, WI	1989 (Jun-Oct)		33	55		6	11		9	15	12		9	8	2	2	423			
Fayette St Park, MI	1989 (Jun-Oct)		10	20		4	7		8	16	9		16	11	6	2	268			
N. Highlands Forest, WI	1984-1985																483	32		∑PCB=95 congeners
Egbert, ON	1988-1989		7		14	8	8	16		5			6							∑PCB=91 congeners
Univ of WI-Green Bay	1988 (Feb)																160			∑PCB=45 congeners
Chicago, IL	1988 (Feb)	174		158	98	25	99	123	22		78		100	112			2300			
0			•	•——	•	•	•	•——	•	•		•	•	•	•——	•	•	•	•	•

Samples collected over the water.

a known human carcinogen. Several POM undergo oxidation in the atmosphere to more toxic forms than that in which they are originally emitted. These oxidation products and their precursors are known mutagens and in some cases, carcinogens. Many POM, including the potential bioaccumulative compounds listed in Table 5-3 are observed at concentrations above detection limits (>0.001 ng/m³) at rural areas in Michigan (Table 5-9).

Table 5-9. The percent of samples with values above the detection limits for polycyclic organic matter at four rural sites in Michigan, 1992-1994.

Compound	Pellston n=79		South Haven n=86		Dexter n=58		Deckerville n=81	
	Particulate	Vapor	Particulate	Vapor	Particulate	Vapor	Particulate	Vapor
Acenapthylene	4	67	1	62	4	79	3	64
Fluorene	28	99	17	98	33	90	14	98
Phenanthrene	20	99	23	100	29	91	7	100
Anthracene	11	27	5	33	7	40	6	28
Fluoranthene	32	67	48	98	35	97	25	88
Pyrene	10	66	23	95	19	93	10	83
Benz(a)anthracene	13	8	30	6	14	5	11	6
Chrysene	23	34	17	41	21	28	9	33
Benzo(b)Fluorene	15	10	27	14	14	17	11	16
Benzo(k)Fluorene	11	22	12	31	12	17	11	27
Benzo(a)Pyrene	14	43	14	49	16	50	11	38
Benzo(g,h,i)Perylene	10	11	4	17	10	19	5	10
2-MeAnthracene	5	56	6	65	7	60	4	56
1-MePhenanthracene	5	43	14	62	5	52	5	40
9-MeAnthracene	4	37	4	38	7	47	5	44

The major source categories for atmospheric POM are stationary fuel combustion (such as electric power generation and residential fuel combustion), industrial operations (including metals processing--especially aluminum production--as well as coke and asphalt production), and transportation. In the Great Lakes region, the areas with elevated POM emissions (3.2 - 6.4 kg/km²/yr) occur along the southern Lake Michigan shore (encompassing the Chicago, Illinois and Gary, Indiana area) and southern Lake Erie. In Michigan, the highest POM emissions occur in southeastern, lower Michigan ranging from 1.6 to 3.2 kg/km²/yr. POM emissions decrease to their lowest values in the Upper Peninsula, ranging from 0.01 - 0.8 kg/km²/yr (Johnson *et al.*, 1992).

Table 5-10 provides mean values for particulate and vapor-phase measurements of low molecular weight POM measured in Michigan from 1992 to 1994. Concentrations for high-molecular weight POM, found mainly in particulate form are presented in Table 5-11, and measurements of the methylanthracene and methylphenanthrene compounds are presented in Table 5-12. The summertime values for POM which were also measured during the LAMUTS of 1991 (Keeler, 1994) are presented in Table 5-13.

## AIR QUALITY STATUS AND EMISSIONS TRENDS

While monitoring of PHAPs has increased over the past five to ten years there are not enough data for most of the pollutants of concern to discuss trends. A strategy to monitor the progress of various programs mandated under the 1990 CAAA and other state and federal programs is needed and may begin under the recently signed Great Lakes Binational Toxics Strategy Agreement.

Table 5-10. Mean, standard deviation and maximum concentrations of particulate and vapor-phase POMs at four rural sites in Michigan, 1992-1994 (ng/m<sup>3</sup>).

Compound		Particulate POM				Vapor Phase POM			
		DEX	DKR	PEL	SHA	DEX	DKR	PEL	SHA
Acenapthylene	MEAN	0.01	0.004	0.01	0.002	0.50	0.28	0.20	0.68
	STD	0.06	0.03	0.06	0.02	0.51	0.51	0.23	0.38
	MAX	0.48	0.29	0.40	0.15	3.50	4.09	1.03	1.74
	Max Date	7Feb92	13Feb94	24Jan93	7Feb94	3Dec93	26Jan94	7Apr93	3Nov93
Fluorene	MEAN	0.12	0.08	0.10	0.08	1.89	1.52	1.04	2.47
	STD	0.28	0.26	0.26	0.27	2.13	1.35	0.68	1.57
	MAX	1.24	1.48	1.48	2.06	10.30	6.79	3.19	8.15
	Max Date	15Oct92	26Jan94	9Sep92	13Feb94	5Jun92	22Aug92	14Dec92	12Jan93
Phenanthrene	MEAN	0.09	0.03	0.11	0.10	1.88	1.18	0.77	2.88
	STD	0.23	0.13	0.27	0.27	2.28	1.12	0.57	2.66
	MAX	1.13	0.85	1.42	1.44	12.78	4.99	2.63	17.98
	Max Date	20Jan94	13Feb94	3Oct92	20Jan94	5Jun92	22Aug92	25Feb94	24Jul93
Anthracene	MEAN	0.02	0.02	0.05	0.01	0.20	0.07	0.07	0.17
	STD	0.11	0.07	0.16	0.06	0.43	0.16	0.14	0.41
	MAX	0.69	0.47	1.17	0.37	2.55	0.73	0.87	2.13
	Max Date	21Nov93	1Feb94	14Dec92	12Feb93	20Jan94	20Dec92	13May93	23Jul92
Fluoranthene	MEAN	0.13	0.07	0.12	0.49	0.54	0.32	0.19	0.98
	STD	0.30	0.15	0.24	1.50	0.54	0.31	0.18	2.08
	MAX	1.42	0.84	1.32	11.53	1.94	1.32	0.77	16.60
	Max Date	11Jun92	13Feb94	25Feb94	6Jun93	29Jun92	11Aug93	23Jun92	24Jul93
Pyrene	MEAN	0.08	0.03	0.04	0.25	0.40	0.29	0.31	0.56
	STD	0.22	0.11	0.15	1.56	0.44	0.32	0.35	1.13
	MAX	1.15	0.73	1.09	14.82	1.90	1.56	1.41	10.71
	Max Date	20Jan94	1Feb94	25Feb94	6Jun93	29Jun92	26Dec92	18Jul93	6Jun93

DEX=Dexter; DKR=Deckerville; PEL=Pellston; SHA=South Haven

Table 5-11. Mean, standard deviation and maximum concentrations of POMs at four sites in **Michigan** 

1992-1994 (ng/m<sup>3</sup>).

Compound	Particulate and Vapor Phase POM Summed							
		DEX	DKR	PEL	SHA			
Benzo(a)anthracene	MEAN	0.07	0.06	0.06	0.33			
	STD	0.23	0.22	0.19	2.05			
	MAX	1.17	1.42	1.03	19.6			
	Max Date	11-Jun-92	13-Feb-94	25-Feb-94	6-Jun-93			
Chrysene	MEAN	0.40	0.10	1.17	0.34			
	STD	1.35	0.20	6.18	1.34			
	MAX	7.74	1.03	55.1	11.6			
	Max Date	13-Jan-93	7-Feb-94	8-Nov-92	6-Jun-93			
Benzo(b)fluoranthene	MEAN	0.15	0.76	1.59	1.23			
	STD	0.74	6.43	8.08	6.76			
	MAX	6.71	63.7	51.1	58.90			
	Max Date	21-Oct-92	9-Oct-92	11-Aug-93	11-Jul-92			
Benzo(k)fluoranthene	MEAN	0.18	1.30	2.75	2.23			
	STD	0.60	11.1	13.6	11.4			
	MAX	3.83	110.1	82.5	98.04			
	Max Date	21-Nov-93	9-Oct-92	11 Aug '93	11-Jul-92			
Benzo(a)pyrene	MEAN	0.35	0.59	1.84	0.71			
	STD	0.68	2.29	7.26	2.29			
	MAX	3.32	19.7	46.7	20.13			
	Max Date	26-Jan-94	9-Oct-92	21-Oct-92	11-Jul-92			
Benzo(ghi)perylene	MEAN	0.41	0.23	0.30	0.21			
	STD	1.18	0.81	1.03	0.53			
	MAX	6.25	5.81	8.31	2.71			
	Max Date	31-May-93	26-Jan-94	26-Jan-94	25-Feb-94			

DEX=Dexter; DKR=Deckerville; PEL=Pellston; SHA=South Haven

Table 5-12. Mean, standard deviation and maximum concentrations for two sites in Michigan from 1993-1994 (ng/m³).

Particulate and Vapor Phases Summed								
		DEX	DKR	PEL	SHA			
2-Methylanthracene	MEAN	0.77	0.77	0.87	1.96			
	STD	0.96	0.74	0.85	6.25			
	MAX	3.14	3.27	4.78	43.5			
	Max Date	7-Feb-94	5-Aug-93	1-Feb-94	24-Jul-93			
1-Methylphenanthrene	MEAN	0.27	0.18	0.21	0.61			
	STD	0.35	0.19	0.28	1.69			
	MAX	1.24	0.75	1.49	9.90			
	Max Date	18-Jun-93	12-Jun-93	29-Aug-93	24-Jul-93			
9-Methylanthracene	MEAN	0.74	0.46	0.34	0.62			
	STD	1.29	0.92	0.73	1.62			
	MAX	5.86	4.40	3.67	10.7			
	Max Date	3-Dec-93	13-Feb-94	25-Feb-94	24-Jul-93			

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Table 5-13. Comparison of mean POM concentrations (sum of particulate & vapor phases) at four Michigan sites with concentrations at LMUATS sites during summer (ng/m³).

	LMUATS Sites					Michigan Sites			
	Chicago, Illinois 1991	Kankake e, Illinois	R/V Laurentia n 1991	South Haven 1991		South Haven 1992-	Dexter	Decker -ville 1992-	Pellston 1992-93
n	16	1991 16	12	18		93 26	3 29	93 29	27
Acenpthylene	4.79	2.61	1.41	0.49		0.23	0.22	0.25	0.15
Fluorene	53.7	3.69	7.17	3.45		3.31	2.87	1.83	1.26
Phenanthrene	167.9	7.97	10.78	4.81		4.28	2.59	1.22	0.77
Anthracene	7,59	0.30	0.27	0.13		0.30	0.12	0.11	0.07
Pyrene	23.6	1.11	1.60	0.77		0.65	0.57	0.05	0.04
Chrysene	5.17	0.33	0.62	0.31		0.07	0.28	0.05	0.04
Benzo(a) Pyrene	3.04	0.26	0.25	0.14		1.14	0.12	0.14	0.77

### CONCLUSIONS AND RECOMMENDATIONS

The PHAPs occur at levels in rural areas that are frequently above the current detection limits and in some cases show large spatial variability depending on proximity to major industrial areas and/or local influences. This observation is cause for some concern, especially since the cycling of these compounds in ecosystems of the Great Lakes has not been elucidated and the very low atmospheric levels are, for some PHAPs, acknowledged as the major source of these contaminants in fish. Synergistic effects, additive effects, and non-cancer endpoints due to exposure to these toxins are largely unexplored. From the limited amount of data in the region, it is clear that rural "hot spots" for some of the persistent pollutants such as DDT exist in Michigan. Identification of these areas is necessary in order to accurately estimate exposures and assess risk.

The identification of sources and an understanding of the deposition, fate and impact of the PHAPs found in the Great Lakes region should be a priority. Although the use of, and concentrations of, many of the persistent pollutants have declined, little information exists on the history and status of these formerly airborne substances in Michigan's ecosystem. The risk of persistent airborne substances goes beyond the Great Lakes alone.

Present and proposed pollution control programs focus on controlling introduction of individual substances while ignoring the interrelated and interdependent factors which impact overall ecosystem conditions. In order to understand the risk airborne substances represent, a program is needed which considers the broad systematic view of the impacts on the state's ecosystem.

PHAPs in Michigan are of concern now and will continue to be in the future. Although the USEPA is expected to develop guidelines for 30 hazardous air pollutants emitted from sources, this falls short of what is needed to understand whether or not these substances have an impact on the ecosystem or whether such control measures are adequate to remediate inland ecosystem damage.

The Trace Metals Relative Risk Task Force recently released its report, entitled *Trace Metals in Michigan's Ecosystem* which provides guidance on an approach which could provide valuable information on the impact of atmospheric transport and deposition (Evans *et al.*, 1998).

The report proposes selection of a series of aquatic ecosystems across the state where the air, land, water, and biota components of each ecosystem would be longitudinally sampled, evaluated and compared. Examination of trace metals and other pollutants in tree rings, soil profiles and sediment profiles would reveal deposition rates as well as background concentrations. Lake sediments, for example, could provide not only a deposition profile but also a measure of the ecosystem response associated with the deposition. Three animal species (fish, turtles and raccoons) could be used as biomonitors to record, statewide, the accumulation and impact of persistent hazardous materials. Correlation of environmental deposition with accumulation in these species would permit an evaluation of the significance of introduced materials to the ecosystem and the response of the system to control or remediate the suspect toxic condition.

In order to implement beneficial control measures, a program needs to be in place to evaluate whether or not an effect is occurring and having a desirable impact on the ecosystem. There is sufficient scientific uncertainty about the role of the PHAPs to warrant consideration of an ecologically-based monitoring program to provide data on the transport and fate of these materials in urban as well as rural areas of the state. The Task Force recommends consideration of such an approach.

### **CHAPTER 6. SULFUR DIOXIDE**

The 1992 Michigan Environmental Relative Risk Analysis project (Rustem *et al.*, 1992a), identified "Criteria and Related Air Pollutants" as being in the medium relative risk category. The criteria pollutants included in this were carbon monoxide, sulfur dioxide, nitrogen dioxide and particulate matter. In the final report it was concluded that because of existing control programs the criteria pollutants occur in Michigan in concentrations lower than the federal standards. Since there was some debate during the original assessment project about the actual existence of a problem or the number of individuals affected, this chapter reviews the current status of the ambient sulfur dioxide issue in the state of Michigan.

Sulfur dioxide ( $SO_2$ ) is a colorless gas at normal ambient temperatures. It has a pungent odor detectable at a concentration of 0.5 ppm. Sulfur dioxide can be oxidized in the atmosphere to form sulfuric acid ( $H_2SO_4$ ), one of the compounds that is responsible for acid deposition. Sulfuric acid and its reaction products with ammonia are the most common fine particulate sulfates found in the ambient air.

The largest sources of SO<sub>2</sub> nationwide are coal burning power plants. Sulfur dioxide is also emitted from non-ferrous smelters, iron ore smelters, petroleum refineries, pulp and paper mills, and steel mills. Area sources include residential, commercial and industrial space heating. Volcanic eruptions are natural sources of SO<sub>2</sub> (USEPA, 1994c).

## SULFUR DIOXIDE EFFECTS

Exposure to SO<sub>2</sub> can aggravate existing pulmonary disease. Asthmatics, children and the elderly are also sensitive to its effects. Sulfur dioxide and particulate matter may exert synergistic toxic effects.

Sulfuric acid formed in the atmosphere is a component of acid deposition and may cause acidification of poorly buffered soil and water, and erosion of building surfaces. Sulfate compounds also contribute to regional haze (USEPA, 1994a).

# NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS) FOR SULFUR DIOXIDE

There are two primary health related NAAQSs for  $SO_2$ : an annual arithmetic average and a 24-hour average. There is also a secondary three-hour average NAAQS for  $SO_2$ . The annual arithmetic average  $SO_2$  NAAQS is 80  $\mu g/m^3$  (0.03 ppm) and the 24-hour average  $SO_2$  NAAQS is 365  $\mu g/m^3$  (0.14 ppm) that may be exceeded no more than once per year. The secondary three-hour average  $SO_2$  NAAQS is 1300  $\mu g/m^3$  (0.50 ppm) that may be exceeded no more than once per year.

Based on a review of the scientific data, the USEPA announced (USEPA, 1996c) on May 22, 1996, that "revisions of the NAAQS for sulfur dioxide are not appropriate at this time." However, the USEPA has decided to provide guidance to assist states in

addressing the potential exposure of sensitive individuals to short-term (5-minute) peaks of  $SO_2$  above 0.6 ppm, even though this does not pose a broad public health problem.

#### MONITORING AND ATTAINMENT STATUS IN MICHIGAN

Figure 6-1 shows the locations of SO<sub>2</sub> ambient monitoring stations that are presently operating in Michigan. There are currently 17 active SO<sub>2</sub> monitoring locations. Of these stations, three are industrial sites, 11 are located within the Detroit Metropolitan Statistical Area (MSA) and three are located outside these areas. Three sites operated by the state are designated as National Air Monitoring Stations (NAMS), which are part of the USEPA's national ambient monitoring network. Seven other sites operated by the Michigan Department of Environmental Quality (MDEQ) are classified as state and Local Air Monitoring Stations (SLAMS). These monitoring locations are operated as part of Michigan's Air Sampling Network required by the USEPA.

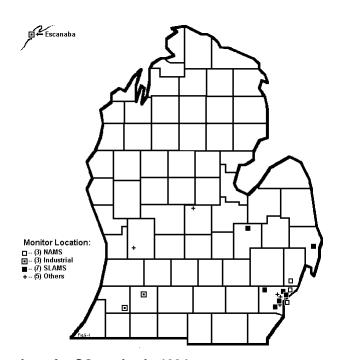


Figure 6-1. Air quality monitors for SO<sub>2</sub> active in 1994.

The majority of the  $SO_2$  monitoring stations sample air on a neighborhood scale to provide an indication of population exposure to  $SO_2$ . These stations include Allen Park, Flint, Grand Rapids, Livonia, Warren and three Detroit stations (Linwood, Temple, and East Seven Mile). Some stations have also been sited to determine maximum  $SO_2$  concentrations that occur within neighborhood scale air masses. Alma, Port Huron and River Rouge measure maximum concentrations from nearby point sources. The site at W. Fort St. in Detroit has been located to monitor the expected maximum  $SO_2$  levels in southeast Michigan.

By October 20, 1982, the entire state was attaining the NAAQS for SO<sub>2</sub> (MDNR,1994). The state has continued to maintain attainment status since that date. Michigan's regulations, which require the use of low-sulfur coal in all power plants, have contributed to this on-going attainment status.

While all areas of the state are currently designated as attainment for  $SO_2$  and monitoring data show the NAAQS is being met, dispersion modeling in a portion of Wayne County indicates the NAAQS could be exceeded if all sources in the area emitted  $SO_2$  at their allowed emission rate. The MDEQ and the affected sources are addressing this issue by adopting site-specific changes to each affected source's  $SO_2$  emission limitations. These changes are expected to be completed soon and will assure that attainment of the NAAQS will be maintained under all possible operating conditions.

### AIR QUALITY AND EMISSION TRENDS

As shown in Figure 6-2, the average  $SO_2$  concentrations across the state are well below the NAAQS (MDEQ, 1996a). A slight increase in the average annual mean concentrations was observed in 1989 and 1990. The average annual mean concentration then declined until 1992 when it leveled off at about 15  $\mu$ g/m³. The mean for 474 sites nationwide was approximately 26  $\mu$ g/m³ in 1984 (USEPA, 1994b). In 1993, this average was about 21  $\mu$ g/m³.

Emissions of  $SO_2$  in the U.S. dropped dramatically during the 1970's and early 1980's and have leveled off since then. The acid deposition provisions of the Clean Air Act Amendments (CAAA) which established the  $SO_2$  allowance program for electric utilities, are designed to reduce United States emissions to ten million tons lower than the 1980 levels. Therefore, ambient  $SO_2$  levels should continue to decrease.

Trends in the 24-hour mean concentrations have followed a similar pattern, as shown in Figure 6-3, with a slight increase in average concentrations during 1989 and 1990. The average 24-hour concentrations have leveled off during 1993 to a statewide average of about 70  $\mu g/m^3$ . In 1989 and 1990, 24-hour values of SO<sub>2</sub> above the level of the NAAQS were measured at an industrial site in Escanaba. The problem was corrected and since that time measured maximum SO<sub>2</sub> levels (24 hour readings) have declined below values recorded during the mid 1980's.

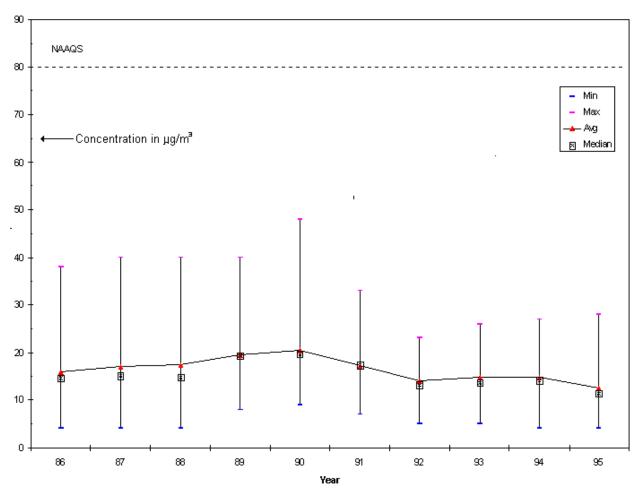


Figure 6-2. Range of SO<sub>2</sub> annual arithmetic means (all sites in Michigan

## TRENDS BY METROPOLITAN STATISTICAL AREAS

In Figure 6-4, the mean of the annual average  $SO_2$  concentrations for all MSA's that implemented monitoring for  $SO_2$  in Michigan are compared. The highest annual average concentrations were detected in Detroit in the late 1980's when the average was about 25  $\mu g/m^3$ . Ambient concentrations declined in the early 1990's and have been consistently under 20  $\mu g/m^3$ . The Grand Rapids/Holland MSA shows an almost steady decline in the annual  $SO_2$  levels. Monitoring in Kalamazoo has shown annual average concentrations below 15  $\mu g/m^3$  throughout the 1990's. Concentrations in 1995 dropped below ten  $\mu g/m^3$  in Flint.

In Figure 6-5, the SO<sub>2</sub> concentrations for each MSA are expressed in terms of the 24-hour average. Saginaw/Midland/Bay City observed the highest concentrations during 1987 and 1988. In 1989, concentrations dropped again. The Kalamazoo MSA has had an upward trend in the 24-hour values, but levels were down in 1995. Flint, Detroit,

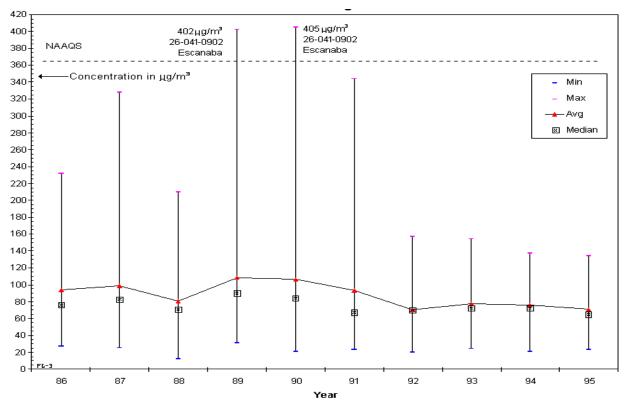


Figure 6-3. Range of maximum 24-hour SO<sub>2</sub> levels (all stations in Michigan).

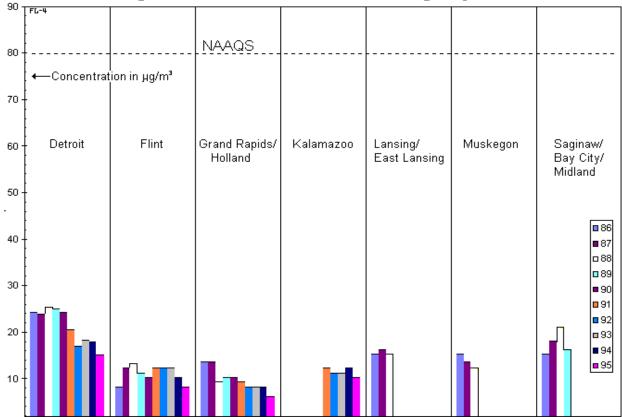


Figure 6-4. Annual mean SO<sub>2</sub> levels by Metropolitan Statistical Areas.

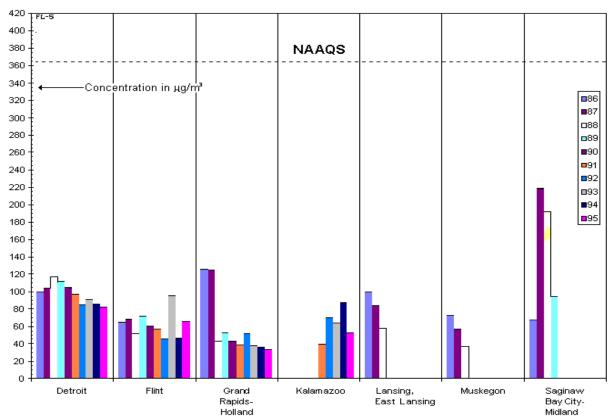


Figure 6-5. SO<sub>2</sub> levels by Metropolitan Statistical Areas, maximum 24 hour mean.

Lansing and Muskegon measurements have all shown a downward trend. Grand Rapids observed levels of about 90  $\mu g/m^3$  in 1986 and 1987 but then underwent a dramatic decline to about 40  $\mu g/m^3$  where it has remained since then.

#### CONCLUSIONS AND RECOMMENDATIONS

Ambient monitoring data shows that Michigan is attaining the NAAQS for SO<sub>2</sub>. Further, in anticipation of USEPA guidance related to the exposure of sensitive individuals to a five minute peak SO<sub>2</sub> concentration greater than 0.6 ppm, the MDEQ initiated a preliminary review of the issue. Based on the location of the source categories the USEPA has targeted, the potential health risk to asthmatics in the state should be limited. No short-term ambient monitoring data for SO<sub>2</sub> are available in Michigan because special monitors with rapid response times are required to accurately record these levels. However, even with this limitation it is possible to review recording charts of the data collected by the existing monitors for an indication of whether or not high, short-term peaks of SO<sub>2</sub> have occurred. Using this technique, the MDEQ reviewed data from St. Clair County, an area with several large SO<sub>2</sub> sources. Until changes to the recording mechanism were made in September 1996, the maximum SO<sub>2</sub> concentration that could be recorded on the St. Clair County recording chart was 0.45 ppm. The data review indicated that short-term peaks above 0.45 ppm can occur one to two times per year. However, until monitoring is conducted with the modified instrumentation

(capable of recording concentrations up to 1.0 ppm), it is unknown if short-term levels in the range of concern are being experienced at this location in Michigan.

The existing regulatory mechanisms for both new and existing sources, coupled with further emission reductions due to the acid deposition provisions of the federal Clean Air Act, appear to be sufficient to prevent any future violations of the NAAQS. With respect to the potential exposure of sensitive individuals to short-term peak sulfur dioxide concentrations, available monitoring data is not capable of determining if concentrations at levels of concern (0.6 ppm) are occurring in Michigan. However, if such levels are identified in the future, the USEPA will provide an appropriate mechanism for the state to address the problem.

Based on continued satisfactory SO<sub>2</sub> air quality and a projected decrease in future SO<sub>2</sub> emissions, the Task Force recommends that no additional specific regulatory action is needed regarding SO<sub>2</sub>.

## **CHAPTER 7. ACID DEPOSITION**

The 1992 Michigan Relative Risk Analysis project (Rustem *et al.*, 1992a) identified acid deposition as being in the medium relative risk category. In the final report, it was concluded that acid deposition in Michigan results primarily from regional transport, although Michigan does make a contribution. It was also noted that because of the state's initiative in issuing low-sulfur fuel regulations, Michigan's contribution of sulfur dioxide (SO<sub>2</sub>) was greatly reduced. In addition, new federal requirements contained in the Clean Air Act Amendments (CAAA), would significantly reduce the production and transport of the precursors of acid deposition.

## DISCUSSION OF ACID DEPOSITION

The state of the science for acid deposition has been established and documented by the National Acid Precipitation Assessment Program (NAPAP) in its 1992 *Report to Congress* (NAPAP, 1993). Acid deposition is the process by which acidic material from the atmosphere is brought to the surface of the earth. Acid deposition involves anthropogenic and biogenic sources. This process or phenomenon is commonly referred to as acid rain. Acidity is measured on the pH scale. This scale ranges from zero to 14. The lower the value, the more acidic; the higher the value, the more alkaline. A value of 7.0 is defined as being neutral.

Natural rainfall in equilibrium with atmospheric carbon dioxide has a pH of 5.6. This value will vary with geography. In areas with soils high in the basic carbonates, the natural pH can exceed 5.6. In other areas, natural acids (organic acids produced from the oxidation of natural hydrocarbons emitted by vegetation and sulfuric acid formed from the emissions of natural sulfur compounds) can result in a pH as low as 5.0. This indicates that in the absence of anthropogenic influences, rainfall is slightly acidic. Convention defines acid rain as rain having an annual average pH of less than 5.0.

Anthropogenic influences accelerate the acidification of rainfall, clouds and fog. These impacts had been observed as early as 1872 by the English scientist Robert Angus, who noted damage to plants and materials and coined the term "acid rain" (Angus, 1872). The NAPAP has observed variation in the mean pH of rainfall in the U.S., ranging from 5.7 in the northern plains states, 4.5 east of the Mississippi, and 4.1 to 4.2 in western Pennsylvania, eastern Ohio, southwestern New York and northern West Virginia. Measurements of mountain clouds and fog show even lower pH values. Mountain clouds in the Appalachian chain have an average pH of 3.6 versus 4.2 for rain, with the most acidic cloud measured at 2.5 on Whiteface Mountain in New York. The most acid fog recorded, occurred in the Los Angeles basin, having a pH of 1.7 (NAPAP, 1987 and 1991).

Acid deposition is technically defined as the total hydrogen ion loading on a given area over a given period of time, typically one year. This hydrogen ion loading can result from acidic rain, snow, aerosols, fog and gases. Acid deposition can be either wet or dry. Wet deposition occurs through rain or snow, with the principal components being

dissolved sulfuric acid  $(H_2SO_4)$  and nitric acid  $(HNO_3)$ . Dry deposition involves acidic gases or particles from the atmosphere, such as acid sulfate particles, being retained by the earth's surface. On the average in the U.S., dry deposition accounts for about 40 percent of the deposited sulfur and nitrogen on a mass basis.

The chemical precursors responsible for the production of acid deposition are sulfur dioxide, oxides of nitrogen ( $No_x$ ) and volatile organic compounds (VOCs). It is worth noting that these are all pollutants regulated by the federal Clean Air Act for other reasons. These precursors react, independently or in combination, with other compounds present in the atmosphere, and/or in the presence of sunlight, to form acids. These reactions begin upon emission from a source and proceed at varying rates, depending upon the compound, weather and the time of day. Acidic deposition may take place near the source or can involve a receptor tens or hundreds of miles from the source.

## **ACID DEPOSITION EFFECTS**

Acidic deposition continues to affect sensitive forest, soil, and aquatic ecosystems. Multiple stressors, including acidic deposition, continue to threaten the long-term structure, function and productivity of many sensitive ecosystems through changes in chemical composition and nutrient cycling. Significant improvement in ecosystem health associated with recent reductions in the emissions of SO<sub>2</sub> are difficult to detect. The results of further reductions are anticipated to yield greater improvements.

On a regional basis, the general order of importance of pollutants on forested ecosystems is: ozone, acidic deposition, sulfur dioxide, and nitrogen oxides. There remains no evidence of a general, widespread decline of forest tree species caused by acidic deposition. However, recent field studies have indicated that acid deposition, in combination with other stresses, is a factor in the high-elevation red spruce decline in the northeastern U.S. This is attributed to frequent exposure (bathing) of acid clouds. There is no analogous situation in Michigan.

There is evidence that chemical changes have occurred in forest ecosystems to the south of the Great Lakes as a result of elevated levels of acidic deposition. These results support the hypotheses that tree uptake and the cycling of sulfur in litterfall have been directly altered by sulfur deposition.

Soil solution chemistry has been directly altered by sulfur deposition and nutrient leaching deposition has been increased in the Great Lakes region. Estimated wet sulfate deposition increased consistently from the northwest of the state to the southeast. Sulfur accumulation in lower Michigan was found to be elevated. While there is concern that wet deposition may impact factors such as nutrient availability, research is continuing on soil-mediated effects.

The impact of acid deposition is an issue for inland lakes, not the Great Lakes. Changes in surface water chemistry have been monitored at 81 selected sites in the

Northeast and upper Midwest since the early 1980's. Most of the lakes experienced no measurable change in acidity, but sulfate levels decreased and nitrate levels have increased in many waters. The widespread decrease in sulfate concentration in the lakes and streams parallels the general decrease in national emissions of  $SO_2$  since 1980. Of the 11 inland lakes studied in Michigan, four registered increases in sulfate and seven registered decreases. The increases occurred in the western Upper Peninsula. Nitrate levels essentially did not change in any of the 11 lakes.

The concentration-response relationships and human exposures associated with acidic aerosols in the atmosphere are covered in chapter two of this report. Acid deposition is not an issue of concern with respect to human health.

It is estimated that wet and dry acidic deposition accounts for 31 to 78 percent of the dissolution of galvanized steel and copper in outdoor exposures. Metal dissolution rates in urban areas in the northeastern U.S. are about three times the rural rates. Little progress has been made since 1990 toward developing additional quantitative data on exterior paint deterioration rates and life cycles. The spotting of automotive finishes is a relatively newly detected effect of acidic deposition. USEPA studies conducted in conjunction with the automotive industry in several locations east of the Mississippi indicate that the spots are etched into topcoats by the interaction of coatings with sulfur compounds and soil-related particles deposited from the atmosphere. Acidic deposition plays an important role in many forms of irreversible stone decay. The shape of the structure influences the rate of decay. Economic assessments are hindered by the lack of sufficient knowledge regarding the extent to which acidic deposition shortens the lifespan of materials.

#### FEDERAL CLEAN AIR ACT INITIATIVES PERTAINING TO ACID DEPOSITION

# Title IV - Acid Rain

The principal focus of the Title IV Acid Rain Program of the Clean Air Act is the electric utility industry. The Act laid out a two-phased approach for tracking and reducing emissions from fossil fuel burning power plants. Phase I required that the first 111 plants, totaling 263 generating units, covered by the program have continuous emissions monitoring systems (CEMS), operational and certified by December 1993, with the USEPA's certification review being completed by November 1994. Additionally, these listed power plants were required to meet intermediate SO<sub>2</sub> emissions limitations by 1995. Two Michigan units, Campbell Units one and two (Consumers Energy), were on the list of 111. These units were in compliance with the intermediate emissions limitations at the time the Act was promulgated. No other Michigan units were on the Phase I list.

Phase II units are defined as all existing and new generating units with a capacity of 25 megawatts or greater. This includes virtually every fossil fuel generating station on the commercial grid. Phase II units were required to have operating and certified CEMS by

January 1, 1995. In addition, these units face more stringent SO<sub>2</sub> and NO<sub>x</sub> emissions limits, which must be in place by the year 2000.

As of 1994, all  $SO_2$  and  $NO_x$  emissions data from Phase I facilities are based on CEMS. Additionally, as of 1995, all  $SO_2$  and  $NO_x$  data from Phase II facilities are based on CEMS. The implementation of the Title IV requirements is one of the success stories for the USEPA and the regulated community, with regard to the CAAA. While Title IV of the Clean Air Act specifically deals with acid deposition and its precursors, other portions of the Act also deal with sources of acid deposition precursors. These are outlined below.

The ozone nonattainment provisions of Title I specify steps to reduce emissions of VOCs and  $NO_x$ , both precursors of acid deposition. It deals with large portions of the U.S. and impacts a broad spectrum of sources and products, with ramifications that extend nationally in scope. The ozone nonattainment provisions of Title I, in conjunction with Title II (Mobile Sources), will result in significant reductions in acid deposition precursors, through new requirements on manufacturing plants, light and heavy duty motor vehicles, small engines and marine engines.

States with ozone nonattainment areas classified moderate and above are required to be working on plans to reach attainment based on reductions in VOCs and/or  $NO_x$  emissions.

Since the Relative Risk project, Michigan has applied for redesignation of its ten ozone nonattainment counties to attainment for the one-hour ozone standard. Redesignation to attainment has been granted to the seven counties in southeast Michigan and two in west Michigan. The redesignation request is still pending for Muskegon County, on the west side of the state.

The USEPA has finalized a new eight-hour ozone national ambient air quality standard. It is expected that this standard will affect the emissions of precursors of acid deposition.

The issues of ozone nonattainment and the new ozone standard are discussed in more detail in chapter three of this report.

## Title I - Particulate Matter

The USEPA has finalized a new standard based on a smaller particulate size,  $PM_{2.5}$ . It is likely that this standard will entail further emissions limitations on sulfates and nitrates, both of which are precursors of acid deposition. This issue is discussed in detail in chapter two of this report.

# Title II - Sulfur In Diesel Fuel Limitation

Under Title II of the CAAA, Congress authorized a reduction in the allowable sulfur content of diesel fuel intended for use in highway vehicles. This became effective October 1, 1993 when the sulfur content of this category of diesel fuel was limited to 0.05 percent, by weight as stated in the *Federal Register*, May 7, 1992. The USEPA has projected that this rule would result in reductions in sulfur dioxide emissions, from highway vehicles, of at least 310,000 tons per year or 43 percent, in 1995. By the year 2015, these reductions are projected to be at least 542,000 tons per year.

# Title III - Great Waters Study

Title III of the CAAA primarily deals with hazardous air pollutants (HAPs) or air toxics. However one portion of Title III may have an impact on the emissions of a particular precursor of acid rain. Congress authorized the USEPA to conduct a review of the effects of atmospheric deposition on the Great Lakes and coastal waters, including Chesapeake Bay. Chesapeake Bay is being adversely affected by nitrates, some of which enter the watershed by atmospheric deposition. As part of the Great Waters Study, the USEPA is being asked to look at the contributions of coal combustion and long range transport to the deposition of nitrates into the bay.

## AMBIENT CONCENTRATIONS AND DEPOSITION

Data from the National Atmospheric Deposition Program (NADP, 1992) indicated a downward trend in sulfate concentrations at 26 of 33 stations. While nitrate concentrations also dropped at the majority of sites, few of the declines were significant. Sulfate and nitrate ions exhibited their highest levels of both concentration and deposition in the area east of the Ohio River Valley, stretching across Pennsylvania and New York. The western half of the U.S. exhibited the lowest concentration and deposition of sulfate and nitrate. Although upward trends in pH were observed at a majority of stations, few were significant.

NADP (1995) examined precipitation chemistry trends in the U.S. It found decreasing sulfate ion trends at well over half the sites in the nation. For the period 1985 to 1993, 26 sites exhibited increasing trends. The majority of these were located in the Western states. Each of Michigan's five sites exhibited downward trends.

Fewer sites exhibited decreasing trends in nitrate ion concentrations, with very few being statistically significant. In fact, for the period 1985 to 1993 more sites exhibited significant increases than decreases (NAPAP, 1991). Seventy-five percent of the sites exhibiting decreases were in the Eastern states. Seventy-five percent of the sites exhibiting increases were in the Western states. Two of Michigan's five sites exhibited slight increasing trends. These were located in the Northern Lower Peninsula and the Western Upper Peninsula.

Recent estimates of aerosol acidity from Maine southward to the Great Smokey Mountains indicated that the acidity of sulfate aerosols increases from north to south. The sulfate aerosol is nearly fully neutralized in Maine.

## **EMISSIONS DATA AND TRENDS**

In 1990, estimated emissions of sulfur dioxide in the U.S. were 23.3 million tons. This represents about a ten percent decline from 25.7 million tons in 1980. Future emissions of sulfur dioxide, from major point sources, will be capped at about 15 million tons as a result of implementation of the acid rain provisions of the CAAA-1990.

Estimated emissions of nitrogen oxides in the U.S. were 21.6 million tons in 1990. This represents a decline of about six percent from 23.0 million tons in 1980. NAPAP projects that these emissions will continue to decline until the year 2000, after which emissions are expected to increase.

VOC emissions continue to decline. It is estimated that these emissions decreased by 17 percent from 1980 to 1990. Implementation of the CAAA are expected to continue this trend beyond the turn of the century.

Emissions trend data, specific to Michigan's major stationary sources, are presented in Table 7-1. Tables 7-2a and 7-2b present regional emissions trend data for Phase I power plants, by state (USEPA, 1995a; 1995b).

Table 7-1. Michigan state-wide emissions inventory trends for major stationary sources.

Year	SO <sub>2</sub> (tons)	NO <sub>x</sub> (tons)	VOCs (tons)
1989	574,740	382,518	108,904
1990	585,819	406,150	157,185
1991	581,698	353,316	90,235
1992	513,719	360,401	81,060
1993	543,418	355,858	89,568
1994	571,676	416,611	99,263
1995	499,607	337,389	82,736

Table 7-2a. SO<sub>2</sub> emission trend data for selected states, Phase 1 units only (in tons).

STATE	1980	1985	1990	1994
OHIO	1,587,833	1,752,637	1,802,003	1,612,201
INDIANA	1,365,626	1,304,436	1,226,609	991,618
PENNSYLVANIA	747,050	676,092	675,537	630,579
ILLINOIS	782,948	782,373	697,897	603,864
MICHIGAN	52,790	60,530	22,784	23,014

Table 7-2b.  $NO_X$  emission trend data for selected states, Phase 1 units only (in tons).

STATE	1985	1990	1994
OHIO	299,231	306,287	324,863
INDIANA	291,613	300,077	245,043
PENNSYLVANIA	151,630	149,588	193,794
ILLINOIS	194,566	174,712	145,769
MICHIGAN	14,144	14,027	11,539

#### CONCLUSIONS AND RECOMMENDATIONS

Michigan is both a source and a receptor of acid deposition. As a source, it remains significantly ahead of its neighboring industrial states in reducing its emissions, primarily as a result of rules passed more than 20 years ago. This forethought in reducing the allowable sulfur in fuel content for electric generating facilities was recognized by Congress in drafting the CAAA.

As a receptor, Michigan, along with the rest of the eastern one-third of the nation, is subject to rainfall that has an annual average precipitation that is regarded as acidic. This may be impacting the pH of surface waters, particularly in the Upper Peninsula. There may be additional effects on forests, and materials that may be attributed to acid deposition, although these do not appear to be an issue in Michigan. The sources of the precursors of acid deposition received in Michigan are predominantly located in states to the south and west.

Actions to control acid deposition precursors are specifically mandated by the CAAA. These actions are underway and are intended to address the issues Michigan faces as both a source and a receptor. Actions are also being implemented under other facets of the Clean Air Act, which will further reduce emissions of the precursors of acid deposition. Consequently, Michigan should continue to focus its efforts on the implementation of the Clean Air Act, as well as maintain an awareness of the status of implementation by the other industrial states in the region. No additional measures appear to be warranted at this time.

## **CHAPTER 8. CARBON MONOXIDE**

Carbon monoxide (CO) is an odorless, tasteless, colorless, poisonous gas that is produced by incomplete combustion of carbonaceous fuels, which include fossil fuels, wood, and plant materials. It is primarily produced by transportation sources and during fuel-burning for space heating and electrical generation, with transportation being the major source nationwide since 1940. Highway vehicles accounted for 62 percent of the CO emissions nationwide in 1993 (USEPA, 1994c). Some industrial processes, as well as wood, agricultural, and refuse burning also contribute to CO emissions.

Because the majority of CO emissions are related to highway vehicles, ambient concentrations increase during morning and afternoon traffic rush hours, and become even more elevated during traffic jams. Peak CO concentrations typically occur during the colder months of the year when CO automotive "cold start" emissions are greater and night time inversion conditions are more intense.

While the number of vehicle miles traveled nationwide has doubled since 1970, CO emissions from mobile sources have actually decreased over that time and continue to do so. Improved fuel economy of the newer cars has resulted in the national fuel consumption remaining relatively constant since 1988, in spite of the increased miles traveled. In addition, improved vehicle emission controls have been installed on all new cars. As a result the mobile source CO emissions have consistently declined since the 1970's. Without these improved control technologies, the 1993 CO emission levels would have been much higher than actually occurred (USEPA, 1994c).

#### CARBON MONOXIDE EFFECTS

Carbon monoxide enters the bloodstream through the lungs and preferentially binds to hemoglobin in the red blood cells. Hemoglobin normally carries oxygen to organs and tissues, but because CO binds with the hemoglobin 240 times more readily than oxygen, the amount of oxygen distributed throughout the body is reduced. The half life of CO in the bloodstream is three to four hours. The health effects are more severe for those who suffer from cardiovascular disease, especially those with angina and peripheral vascular disease because their circulatory systems are less efficient at carrying oxygen. Healthy individuals are also affected, but at more elevated concentrations (USEPA, 1994b).

Carbon monoxide interferes with mental and physical activity by slowing reactions, impairing vision and judgment, work capacity, manual dexterity, learning ability and performance of complex tasks. Headaches, nausea, vomiting, convulsions and even death can be attributed to very high levels of CO exposure. The severity of the effects is related to the time of exposure and the concentration of the carbon monoxide in the environment.

## NATIONAL AMBIENT AIR QUALITY STANDARDS FOR CARBON MONOXIDE

There are two primary National Ambient Air Quality Standards (NAAQS) for CO; an eight-hour standard of nine ppm, which is about ten mg/m³, and a one-hour standard of 35 ppm or 40 mg/m³ (40 CFR Part 58). There is no secondary standard for CO. The eight-hour standard is considered to be the more restrictive form because there has not been an exceedence of the one-hour standard, on a national level since 1990 (USEPA, 1994c).

The NAAQS for CO were originally established in 1971. The most recent reassessment of the scientific basis of the standards by USEPA and its Clean Air Scientific Advisory Committee (CASAC) in 1992 resulted in the standards being reaffirmed (McClellan, 1992; MDEQ, 1994).

## CARBON MONOXIDE AMBIENT MONITORING IN MICHIGAN

Figure 8-1 shows the locations of CO monitoring stations that are presently in operation in Michigan. Since 1986, ten stations have operated as long term monitoring trend sites. Previously, the maximum number of monitors in operation was 13 in calendar year 1988. Currently, there are ten sites measuring CO concentrations. Of these stations, some are located to detect maximum levels of CO and some are to monitor population exposure to CO. Because high levels of CO are often found near roadways and street canyons, the station at Fort St. in Detroit is sited to detect these "high spikes" in CO concentrations. The site located at 14800 Evergreen in Detroit was selected to measure levels of CO emissions and to determine population exposure from mobile sources. Maximum concentrations from stationary sources are detected at the Alma location. The sites in Grand Rapids, Oak Park, Allen Park, Linwood in Detroit, Livonia and Temple in Detroit were selected to determine population exposure that results from mobile and area source emissions.

## ATTAINMENT/NON-ATTAINMENT STATUS OF CARBON MONOXIDE IN MICHIGAN

The majority of monitoring stations are located in the Detroit Metropolitan Statistical Area (MSA) due to the non-attainment status of portions of Wayne, Oakland and Macomb Counties as shown in Figure 8-2. The specific area corresponds to the area inside the boundaries formed by the route described below (MDEQ, 1994).

## LONG TERM TRENDS IN AMBIENT CARBON MONOXIDE CONCENTRATIONS

As shown in Figure 8-3, ambient CO levels decreased steadily from 1986 until 1988, after which time, both the median and mean one-hour values averaged for all sites operating in the state became relatively constant at about ten ppm, which is less than a third of the NAAQS. The highest one-hour maximum concentration that was detected across the state in the past ten years occurred in 1986 at Warren when a value of 25.4 ppm was measured. Grand Rapids detected a one-hour value of 25.3 during the same

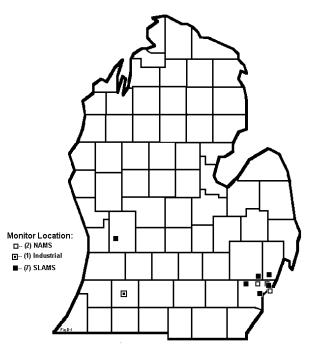


Figure 8-1. Air quality monitors for CO active in 1995.

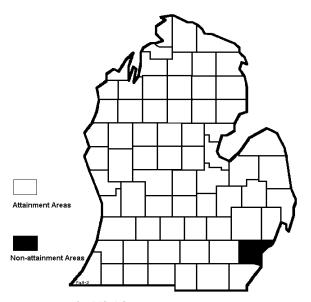


Figure 8-2. CO non-attainment areas in Michigan, 1994.

[(Non-attainment Area: Detroit-Port Huron Air Quality Control Region.) The clockwise route, following Lake St. Clair to 14 Mile Rd. to Kelly Rd., north to 15 Mile Rd. to Hayes Rd., south to 14 Mile Rd. to Clawson City boundary, following north Clawson City boundary to north Royal Oak City boundary to 13 Mile Rd. to Evergreen Rd to southern Bingham Farms City boundary to southern Franklin City boundary to Inkster Rd., south to Pennsylvania Rd. extending east to the Detroit River, defines the study area.]

year. Both of these values are well below the one-hour NAAQS for CO of 35 ppm. However in Michigan, the controlling standard has been the eight-hour average concentration.

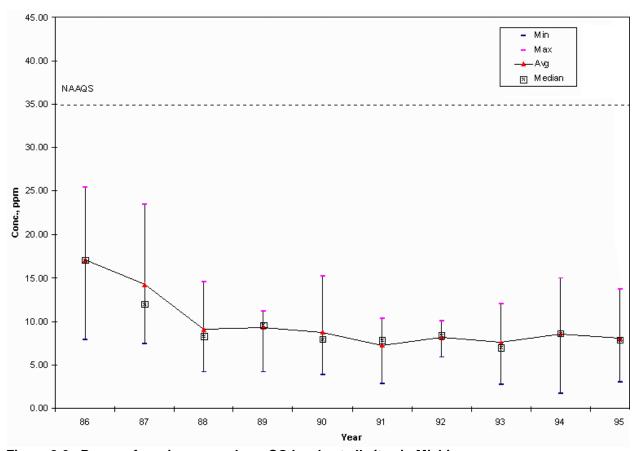


Figure 8-3. Range of maximum one-hour CO levels at all sites in Michigan.

Figure 8-4 indicates that although the median levels of CO measured over an eight-hour time period have decreased from 1986 until 1990, the maximum eight-hour readings still occasionally approach or exceed the NAAQS. In fact, during the 1994 calendar year, the monitor located at Evergreen in Detroit detected CO levels of 10.3 ppm (on January 10, 1994) and 10.7 ppm (on December 23, 1994) over an eight-hour period. During seven of the past ten years, the Evergreen site has detected the highest eight-hour levels of CO measured across the entire state, and averaged 8.4 ppm (standard deviation = 1.8). The average levels for all of the sites in the Detroit MSA is 6.1 ppm (standard deviation 2.1).

Table 8-1 lists historical CO exceedences for the previous ten years. During 1994, there were two exceedences of the national air quality standard at the Detroit Evergreen site. Exceedences were also measured at this site during 1987 and 1988. The highest CO concentration that was detected in Michigan from 1985 until 1995 occurred on January 16, 1986 at Warren. The Warren monitor detected two

exceedences during 1986 and one during 1987, but the air quality near this station has shown improvement since then.

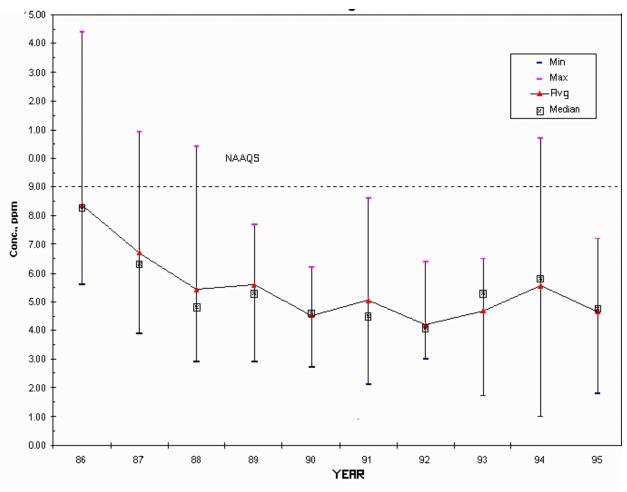


Figure 8-4. Eight-hour median CO levels from 1986 to 1995.

# TRENDS IN AMBIENT CONCENTRATIONS BY METROPOLITAN STATISTICAL AREA

Of the major cities in Michigan that have long term trends in monitoring for CO, the highest levels are in the Detroit MSA. Figure 8-5 compares the second highest annual levels at various MSA's for CO. The Saginaw/Bay City/Midland MSA had the greatest average value (9.3 ppm) in 1985. This dropped 50 percent by 1986, showing a decline and leveling-out trend until monitoring was discontinued in 1991. The Saginaw area monitors were influenced by significant local industrial sources that were controlled in 1986. Similar but less pronounced trends are shown for both Detroit and the Grand Rapids/Holland MSAs. The significant drop in these areas is likely due to better emission controls on mobile sources.

Table 8-1. Values exceeding the eight hour NAAQS (9 ppm) for CO in Michigan from 1985 to 1995.

Year	Total number of	Site	Date	End hour	Max value 8
	exceedences				hr., ppm
1985	1	Saginaw Co.	1/17/85	14	10.0
1986	2	Warren	1/16/86	14 14.4	
		Warren	12/16/86	2	11.9
1987	2	Warren	2/20/87	9	9.6
		Detroit (Evergreen)	10/24/87	6	10.9
1988	1	Detroit (Evergreen)	1/19/88	3	10.4
1989	0				
1990	0				
1991	0				
1992	0				
1993	0				
1994	2	Detroit (Evergreen)	1/10/94	8	10.3
		Detroit (Evergreen)	12/23/94	2	10.7
1995	0				

NAAQS

NA

Figure 8-5. CO levels by MSA (average of second highest eight-hour max.).

## CARBON MONOXIDE EMISSIONS IN MICHIGAN

In 1994, the MDEQ conducted a comprehensive inventory of anthropogenic CO emissions in the seven counties of southeast Michigan that comprise the Detroit/Ann Arbor Consolidated MSA. The inventory included actual CO emissions for the year 1990, and a projection of CO emissions for the years of 1986 and 2006. The 1986 year was selected since it was the last year (at the time of the inventory) to have exceedences of the NAAQS. The year of 1990 was established as the base year and

the year 2006 was selected to consider future emission trends. The year 2006 emission estimates include the impact of both the growth in the area and the effect of implementing the control measures of the Federal Motor Vehicle Control Program. Since exceedences of the NAAQS are most likely to occur in the winter, the inventory is calculated on a winter day basis.

A summary of the CO emissions is shown in Table 8-2. Three source categories stationary point, mobile sources (including both on and off highway sources), and other area sources, are listed. As indicated, mobile sources make-up approximately 90 percent of the total CO emissions. From 1986 to 1990 there was an emission reduction of 17 percent while the projected additional reduction by the year 2006 is 38.5 percent.

Table 8-2: Carbon monoxide emissions southeast Michigan.

Calendar	Emissions (tons per winter day)			
Year	Point Sources	Mobile Sources	Other Area	Totals
1986	284.1	5,498.5	170.2	5,952.8
1990	155.0	4,617.2	165.5	4,937.7
2006	158.2	2,709.4	167.7	3,035.3

## CONCLUSIONS AND RECOMMENDATIONS

In general, air monitoring data collected across the state indicate the NAAQSs for carbon monoxide are being met. While a portion of the Detroit metropolitan area is still designated non-attainment and a violation of the standard occurred within that area in 1994, monitored levels of CO decreased from the mid-1980s to the early 1990s and remained stable since then. Even at the site recording the violation, the NAAQSs have been met five of the past six years.

In addition, since the Clean Air Act requires all non-attainment areas to have plans to bring areas into attainment, the Governor's Steering Committee on Clean Air Act Implementation has considered what action, if any, is necessary to address the issue. The Steering Committee has recommended the following:

- 1. Air Quality agencies in the state should continue to assess the CO status in southeast Michigan. Quantification of the benefits to be derived from all relevant programs should be completed, including but not limited to the following:
- 2. Potential benefits from fuel providers who elect to supply reformulated gasoline,
- 3. Alternative fuel vehicles required under the Energy Policy Act with on-board diagnostics,
- 4. Fleet turnover (cleaner cars),

- 5. Public information on proper vehicle maintenance,
- 6. Reductions that occur under the proposed emission trading program, and
- 7. Possibility of 49-state car program.

An evaluation of the ability to maintain the CO NAAQSs in future years should guide decisions on additional measures. If no additional exceedences of the NAAQS occur before the end of 1997, the MDEQ believes the southeast Michigan area will qualify for redesignation to attainment status. In early 1998 the MDEQ will verify the ambient data and, if appropriate, initiate a redesignation action for USEPA approval.

Therefore, based on the generally satisfactory air quality in Michigan, a projected decrease in future CO emissions, and the recommendations of the Governor's Steering Committee, the Task Force believes that no additional action is needed regarding carbon monoxide.

#### **CHAPTER 9. NITROGEN DIOXIDE**

Nitrogen oxides  $(NO_x)$  are formed during combustion processes that create extremely high temperatures, such as those that result from burning coal, oil and gas fuel and in motor vehicle engines. During the combustion process, nitrogen gas  $(N_2)$  which is a relatively inert gas that makes up approximately 78 percent of the atmosphere, combines with oxygen  $(O_2)$ , another component of the earth's atmosphere (about 21 percent) and forms nitric oxide (NO) and nitrogen dioxide  $(NO_2)$ . Of the total  $NO_x$  emissions,  $NO_2$  accounts for about ten percent and NO 90 percent. Upon release to the atmosphere, photochemically-initiated reactions convert NO to  $NO_2$ . The rate of this conversion is dependent upon the intensity of sunlight and the presence of other substances like ozone and volatile organic compounds (VOCs).

Major sources include electrical power plants, motor vehicles, incinerators, industrial boilers and some chemical processes. Home heaters and gas stoves also produce NO and can be important sources of total NO<sub>2</sub> exposure. Natural emissions from lightning and bacteria found in the soil also contribute nitrogen dioxide to the atmospheric loadings.

## NITROGEN DIOXIDE EFFECTS

At high concentrations, nitrogen dioxide has been shown to cause lung cell injury and other respiratory effects in humans both chronically and acutely. Consequently, a long-term annual average standard has been set to address the chronic exposure, and a short-term, one-hour standard has been considered but not adopted. With respect to welfare effects, the principle concern is that nitrogen deposition could pose threats to some sensitive ecosystems. Another concern is that NO<sub>2</sub> is optically active (i.e., it absorbs visible light and therefore can contribute to reduced visibility and cause a brownish discoloration to the atmosphere). As a result, the recent National Ambient Air Quality Standards (NAAQS) review for NO<sub>2</sub> addressed these issues as well.

# NATIONAL AMBIENT AIR QUALITY STANDARDS FOR NITROGEN DIOXIDE

The NAAQS for  $NO_2$  is an annual average standard of 100  $\mu$ g/m³ or 0.053 ppm. A recent review of the scientific basis for this standard was completed by the USEPA's Clean Air Scientific Advisory Committee (CASAC) in 1995. In its Staff Paper, the USEPA (1995a) concluded that an annual primary standard in the range of 0.05 to 0.08 ppm provides adequate protection against the health effects associated with long-term exposure to  $NO_2$ . It also concluded that if the 0.053 ppm standard is attained, the occurrence of short-term concentrations of concern (1-hr. peaks of 0.2 ppm or higher) would be unlikely in most areas of the country. Regarding a secondary NAAQS for  $NO_2$ , the USEPA concluded that a secondary standard equal to the primary standard would "provide adequate protection against the direct effects of  $NO_2$  on the environment." Further, the USEPA concluded that a secondary NAAQS for  $NO_2$  to protect visibility is

not warranted. In the closure letter, the CASAC endorsed all four of the USEPA's conclusions (Wolff, 1995) .

## CONCENTRATIONS AND TRENDS IN MICHIGAN

In 1995, there were six  $NO_2$  monitoring sites in operation in Michigan and the measured annual averages were only a small fraction of the NAAQS. In 1995, annual averages ranged from less than 0.01 ppm at a site in Benton Harbor to a high of 0.02 ppm at a site in Detroit (MDEQ, 1994b). As expected, the highest ambient concentrations are measured in the Detroit area, but the annual average concentrations have been declining since 1987 (MDEQ, 1994a). Emission projections indicate that total  $NO_x$  emissions in the Detroit area will be about seven percent lower in 2005 than in 1993 (SEMCOG, 1993). The decreasing emissions trend is primarily due to emission reductions already mandated by the Clean Air Act Amendments (CAAA) for motor vehicles and utility boilers. Statewide,  $NO_x$  emission trends have been flat and will likely continue to be flat or decrease slightly due to the 1990 CAAA mandates.

## CONCLUSIONS AND RECOMMENDATIONS

Since March 3, 1978, all of the air quality control regions in Michigan and most of the nation have been in attainment for nitrogen dioxide (MDNR, 1994). According to the 1992 National Ambient Air Quality Trends Report (USEPA, 1994c), the only urban area nationwide that has recorded violations of the NAAQS for NO<sub>2</sub> during the previous ten years was Los Angeles. Since 1992, even Los Angeles has met the NAAQS.

Since the concentrations of  $NO_2$  measured in the state are well below any levels of concern for human or ecosystem health and because the ambient concentration and emission trends are either downward or flat, we conclude that  $NO_2$  does not pose a public health risk or an ecological risk in the state of Michigan. Existing regulations appear to be sufficient so that it will not be a risk in the foreseeable future. Consequently, no additional actions need to be taken.

## CHAPTER 10. MAJOR FINDINGS AND RECOMMENDATIONS

In July 1992, the Michigan Relative Risk Analysis project identified 24 environmental issues of concern in the state of Michigan in a report entitled *Michigan's Environment and Relative Risk*. The issues were classified into one of four relative risk categories: high-high, high, medium-high, and medium. Of the 24 issues, four air quality issues were identified. "Atmospheric transport and deposition of air toxics" was the highest ranked air issue and was ranked in the "high" category. "Photochemical smog" was ranked "medium-high," while "acid deposition" and "criteria and related air pollutants" were rated "medium" risk.

Following the release of the report, Governor John Engler directed the Natural Resources Commission (NRC) to review state environmental programs and to provide recommendations to reduce the risks identified in the relative risk report to acceptable levels. The NRC re-grouped the 24 risk issues into 18 distinct categories to be assigned to separate task forces. The Air Quality Issues Task Force (Task Force) was created on June 30, 1994, and was assigned all of the air quality relative risk issues identified in the report. The Task Force was charged to:

- 1. Determine whether the air quality issues identified in the report are still the appropriate issues of concern,
- 2. Assess whether they pose an unacceptable public or ecological health threat now or will pose such a risk in the near future,
- 3. Judge whether existing federal or state regulations and practices are sufficient to mitigate unacceptable risks, or in the case of risks that are currently acceptable, assess if present regulations are sufficient to prevent the risks from becoming unacceptable in the future, and
- 4. Ascertain if additional measures are required to manage the risk to acceptable levels or to maintain them at acceptable levels.

## ISSUE 1. PARTICULATE MATTER (PM)

At present, all locations within Michigan are meeting the existing PM<sub>10</sub> (particulate matter with a diameter less than or equal to ten micrometers) National Ambient Air Quality Standards (NAAQS), and the trend in PM<sub>10</sub> concentrations continues downward. This trend should continue in the near future because of the implementation of other air pollution control programs that will reduce PM<sub>10</sub> emissions and the emissions of gaseous PM precursors. Consequently, PM<sub>10</sub> does not appear to pose an unacceptable public health risk in Michigan and new control initiatives targeting PM<sub>10</sub> are not warranted. For PM<sub>2.5</sub> (particulate matter with a diameter less than or equal to 2.5 micrometers), the situation is not as simple. The review by the United States Environmental Protection Agency's (USEPA) Clean Air Scientific Advisory Committee (CASAC) demonstrated that there is no scientific consensus on the degree of public

health risk posed by PM $_{2.5}$  at the concentrations believed to be present throughout the U.S. Because no comprehensive national monitoring of PM $_{2.5}$  exists, actual concentration levels for most areas are not known. Specifically, Michigan concentrations are unknown because there are no measurements presently being made by the Michigan Department of Environmental Quality (MDEQ). On balance, more of the CASAC members favored PM $_{2.5}$  NAAQS at levels above those which USEPA has chosen. These members favored PM $_{2.5}$  NAAQS roughly of equivalent stringency as the current PM $_{10}$  NAAQS (approximately 25-30  $\mu$ g/m $^3$ ). At such a level, Michigan would likely be in attainment and the threat posed to public health would be perceived to be acceptable. However, unless the new PM $_{2.5}$  NAAQS are overturned by Congress or in the courts, Michigan will be required to implement additional emission control programs in nonattainment areas even if an unacceptable public health risk has not been demonstrated.

At this point, the Task Force recommends that Michigan not initiate any new control programs that target  $PM_{2.5}$  or  $PM_{2.5}$  precursors until required by federal law. According to the USEPA's implementation schedule, this should not occur until the year 2005. The Task Force does, however, recommend that Michigan begin  $PM_{2.5}$  sampling with speciation as soon as possible. In addition, the Task Force also recommends that Michigan encourage the USEPA to accelerate its  $PM_{2.5}$  health effects research program so that the uncertainties and many unanswered questions raised by CASAC are addressed before the next CASAC PM review is completed in 2002.

## ISSUE 2. GROUND-LEVEL OZONE

Ozone (O<sub>3</sub>) concentrations throughout the state are decreasing and based on emission inventory projections, they should continue to decline in the near future. Maintenance plans that are in effect will insure that precursor emissions will not increase in the future. Presently, Muskegon, Allegan, Oceana and Mason Counties are the only areas in the state still effected by the one-hour NAAQS. While trend lines suggest that these counties will attain the one-hour NAAQS in a few years, it is generally acknowledged that the high ozone in all three counties is due to transport from the Chicago/Milwaukee area and that local emission reductions in Muskegon or other counties would not appreciably impact the ozone locally. However, the emission reductions that will be required in the Chicago/Milwaukee area will be designed to bring Muskegon and the other areas into attainment. Consequently, with regards to the one-hour standard, additional measures beyond managing the programs in place are not necessary.

However, even though public health benefits for a new eight-hour standard at 0.08 ppm have not been demonstrated, the USEPA has adopted it and numerous counties in southern Michigan will not meet it. Numerous organizations have filed lawsuits against the USEPA to prevent implementation of the new standard. If it is implemented, widespread emission reductions of precursor emissions will be necessary for these counties to come into compliance.

At this point, the Task Force recommends that Michigan not initiate any new control programs that target  $O_3$  precursors until they are required to do so. However, this could happen as early as the year 2002 if Michigan is required to implement the USEPA's regional transport strategy for the eastern United States.

# ISSUE 3. HAZARDOUS AIR POLLUTANTS (HAPS)

"The chemicals defined in the chapter as HAPs are potential public health concerns and include the 188 compounds identified in the 1990 CAAA and the over 750 compounds for which screening levels have been developed under the Michigan air toxic rules. Due to the CAAA and the MDEQ air toxic program, major sources of HAPs have been identified and subjected to federal and state regulations. However, because of errors in the ambient air monitoring database, an assessment of the relative risk associated with the HAPs is not possible. The Task Force recommends that the MDEQ makes it a high priority to determine what data from the existing monitoring database is correct and of high quality and to collect additional high quality ambient air HAPs so that such an assessment can be conducted in the near future. The Task Force further recommends that the existing federal and state programs to reduce HAPs be continued while the ambient air assessment is being conducted."

# ISSUE 4. PERSISTENT HAZARDOUS AIR POLLUTANTS (PHAPS)

The PHAPs include approximately a dozen chemicals identified by the USEPA which have long environmental lifetimes and pose both a public health and ecosystem risk because they accumulate in the food chain of the Great Lakes' ecosystems. The PHAPs occur at levels in rural areas that are frequently above the current detection limits and in some cases show drastic spatial variability depending on proximity to major industrial areas and/or local influences. This observation is cause for some concern, especially since the cycling of these compounds in ecosystems of the Great Lakes has not been elucidated and the very low atmospheric levels are, for some PHAPs, acknowledged as the major source of these contaminants in fish. Synergistic effects, additive effects, and non-cancer endpoints due to exposure to these toxins are largely unexplored. From the limited amount of data in the region, it is clear that rural "hot spots" for some of the PHAPs, such as DDT, exist in Michigan. Identification and characterization of these areas is necessary in order to better estimate exposures and assess risk.

The identification and characterization of atmospheric sources, sinks and transport mechanisms for the PHAPs present in the Great Lakes airshed should be a priority. This is in line with currently mandated efforts by the USEPA which must identify and develop guidelines for the top 30 HAPs from area sources (those which emit less than ten tons of any one HAP or less than 25 tons of a combination of HAPs). The PHAPs in Michigan will continue to be of concern in the future until their chemistry, sources and transport are better understood in urban as well as in rural areas of the state.

In order to implement beneficial control measures, a program needs to be in place to evaluate whether or not an effect is occurring and having a desirable impact on the ecosystem. There is sufficient scientific uncertainty about the role of the PHAPs to warrant consideration of an ecologically-based monitoring program to provide data on the transport and fate of these materials in urban as well as rural areas of the state. The Task Force recommends consideration of such an approach.

## ISSUE 5. SULFUR DIOXIDE

Air monitoring data show that the NAAQS for sulfur dioxide (SO<sub>2</sub>) are being met throughout Michigan. Further, the existing regulatory mechanisms for both new and existing sources, coupled with further emission reductions due to the acid rain provisions of the Clean Air Act, appear to be sufficient to prevent any future violation of the NAAQS. With respect to the potential exposure of sensitive individuals to short-term peak sulfur dioxide concentrations, available monitoring data is not capable of determining if levels in the range of concern to the USEPA are occurring in Michigan. However, if such levels are identified in the future, the USEPA will provide an appropriate mechanism for the state to address the problem.

Based on continued satisfactory air quality and a projected decrease in future SO<sub>2</sub> the Task Force believes that no additional specific action is needed regarding sulfur dioxide.

## ISSUE 6. ACID DEPOSITION

Michigan is both a source and a receptor of acid deposition. As a source, it remains significantly ahead of its neighboring industrial states in reducing its emissions, primarily as a result of rules adopted more than 20 years ago. This forethought in reducing the allowable sulfur in fuel content for electric generating facilities was recognized by Congress in drafting the CAAA.

As a receptor, Michigan, along with the rest of the eastern one-third of the nation, is subject to rainfall that has an annual average precipitation that is regarded as acidic. This may be impacting the pH of surface waters, particularly in the Upper Peninsula. There may be additional effects on forests, and materials that may be attributed to acid deposition, although these do not appear to be an issue in Michigan. The sources of the precursors of acid deposition received in Michigan are predominantly located in states to the south and west.

Actions to control acid deposition precursors are specifically mandated by the CAAA. These actions are under way and are intended to address the issue Michigan faces as both a source and a receptor. Actions are also being implemented under other facets of the Clean Air Act, which will further reduce emissions of the precursors of acid deposition. Consequently, Michigan should continue to focus its efforts on the implementation of the Clean Air Act, as well as maintain an awareness of the status of

implementation by the other industrial states in the region. No additional measures appear to be warranted at this time.

#### ISSUE 7. CARBON MONOXIDE

Air monitoring data collected across the state indicate the NAAQS for carbon monoxide (CO) is being met. While a portion of the Detroit metropolitan area is still designated non-attainment and a violation of the standard occurred within that area in 1994, monitored levels of CO decreased from the mid-1980s to the early 1990s and remained stable since then. Even at the site recording the violation, the NAAQS have been met five of the past six years. Based on this information, the MDEQ now believes the area qualifies for redesignation to attainment and will be initiating such action in the near future.

Since the Clean Air Act requires all non-attainment areas to have plans to bring areas into attainment, the Governor's Steering Committee on Clean Air Act Implementation has considered what action, if any, is necessary to address the issue. The Steering Committee has recommended that air quality agencies in the state should continue to assess the CO status in southeast Michigan. Quantification of the benefits to be derived from all relevant programs should be completed. The Steering Committee also recommended that an evaluation of the ability to maintain the CO NAAQS in future years should guide decisions on additional measures.

Therefore, based on the generally satisfactory air quality, a projected decrease in future CO emissions, and the recommendations of the Governor's Steering Committee, the Task Force believes that no additional action is needed regarding carbon monoxide.

#### ISSUE 8. NITROGEN DIOXIDE

Since March 3, 1978, all of the air quality control regions in Michigan and most of the nation have been in attainment for nitrogen dioxide (NO<sub>2</sub>). The only U.S. urban area that has recorded violations of the NAAQS for NO<sub>2</sub> the previous ten years was Los Angeles, but by 1992, even Los Angeles met the NAAQS.

Since the concentrations of  $NO_2$  measured in the state are well below any levels of concern for human or ecosystem health and because the ambient concentration and emission trends are either downward or flat, the Task Force concludes that  $NO_2$  does not pose a public health risk or an ecological risk in the state of Michigan. Existing regulations appear to be sufficient so that it will not be a risk in the foreseeable future. Consequently, no additional actions need to be taken.

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#### **APPENDIX**

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